

could lead one to conclude that the nature of the magnetic interaction that leads to these phenomena is of the same physical origin. Graphical analysis of the low-temperature resistance characteristics of dilute Zn-Mn alloys, assuming the sum of two terms; one due to magnetic ordering and one due to resonance scattering results in a value of  $J$  in agreement with that derived from other transport phenomena. This then suggests a method of separating the resistance minimum from

total resistivity in the presence of a resistance maximum produced by magnetic ordering.

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### Covalency in Crystal Field Theory: $\text{KNiF}_3$

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The theory of covalency in crystal field phenomena is examined, using, as example, the  $\text{Ni-F}_6$  complex in  $\text{KNiF}_3$ . The Hund-Mulliken-Van Vleck molecular orbital-linear combination of atomic orbitals treatment is followed. The role of the antibonding *and* bonding electrons in the complex is discussed from a multi-electron point of view. The exact self-consistent one-electron Hamiltonian is discussed in some detail. Emphasis is placed on elucidating the source and nature of the covalent effects appropriate to the various physical phenomena. We find that it is the covalent mixing of those *bonding* electrons having no antibonding partners which contribute to all experimental observables (including the crystal field splitting  $10 Dq$ , transferred hyperfine interactions, neutron magnetic form factors, and superexchange interactions). This view of covalency differs markedly from the one followed by Sugano and Shulman, in that the covalency of the *antibonding* electrons, which are assigned the sole role in their approach, is totally irrelevant. Quantitative numerical estimates (using approximations to the exact Hamiltonian) are given for the two models of the covalent effects in  $\text{KNiF}_3$ , i.e., "unpaired" bonding and antibonding; they are shown to differ strongly. The relative roles of overlap and covalency are discussed; covalency is found to play an important but by no means dominant role. Numerical agreement between the present inexact cluster theory and experiment is found to be poor. The various sources of this disagreement are reviewed.

#### I. INTRODUCTION

CRYSTAL field theory<sup>1,2</sup> has had a long and varied history: when treated as a semiempirical theory, with the crystal field splitting  $10 Dq$  considered as an adjustable parameter, it has been highly successful in fitting experimental data; when considered as a fundamental theory for the behavior of transition metal ions in crystalline fields, it has been strikingly unsuccessful in predicting, from first principles, the fundamental parameter  $10 Dq$ . Following the pioneering computations of Van Vleck<sup>3</sup> and Polder,<sup>4</sup> a series of theoretical investigations<sup>5-9</sup> succeeded in pinpointing the basic

shortcomings of the theory, and indicated the need for a multielectron many-center molecular approach.

The recent work of Sugano and Shulman<sup>10</sup> (henceforth denoted as S&S III), representing the most detailed computations undertaken to date, attempted to obtain a quantitative basis for the theory by including all the terms in the ionic model considered by their predecessors, as well as the effect of metal ion-ligand covalent mixing. A cluster model consisting of the metal ion and its nearest ligand neighbors in an external Madelung-like potential was invoked. Considering  $\text{KNiF}_3$ , they obtained a theoretical cubic field splitting parameter ( $10 Dq$ ) for Ni which gave the first quantitative indication that covalency plays an important role in the crystal field interactions of salts as highly ionic as

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<sup>1</sup> H. Bethe, *Ann. Physik* **3**, 133 (1929).

<sup>2</sup> J. H. Van Vleck, *Phys. Rev.* **41**, 208 (1932).

<sup>3</sup> J. H. Van Vleck, *J. Chem. Phys.* **7**, 72 (1939).

<sup>4</sup> D. Polder, *Physica* **9**, 709 (1942).

<sup>5</sup> W. H. Kleiner, *J. Chem. Phys.* **20**, 1784 (1952).

<sup>6</sup> H. S. Jarrett, *J. Chem. Phys.* **31**, 1579 (1959).

<sup>7</sup> Y. Tanabe and S. Sugano, *J. Phys. Soc. Japan* **11**, 864 (1956).

<sup>8</sup> J. C. Phillips, *Phys. Chem. Solids* **11**, 26 (1959).

<sup>9</sup> A. J. Freeman and R. E. Watson, *Phys. Rev.* **120**, 1254 (1960). This reference also contains a useful review of the theoretical investigations prior to the work of Ref. 10.

<sup>10</sup> S. Sugano and R. G. Shulman, *Phys. Rev.* **130**, 517 (1963); henceforth denoted as S&S III.

$\text{KNiF}_3$ . In addition, they considered the role of the computed covalent mixing in the  $\text{F}^{19}$  transferred hyperfine interactions.<sup>11</sup>

While the role of covalency in superexchange,<sup>12</sup> and transferred hyperfine effects<sup>11,13-17</sup> have been particular objects of study, overlap and covalent mixing significantly affect almost every observable in an iron series salt. Covalent behavior must be understood in detail before matters such as the theory of superexchange can be put on any sort of quantitative basis.

Sugano and Shulman's modification of crystal field theory to include covalency in the cluster model may be viewed as an extension of the traditional approach to crystal field effects in ionic salts. In  $\text{KNiF}_3$ , the familiar triply ( $t_{2g}$ ) and doubly ( $e_g$ ) degenerate  $3d$  orbitals, describing the  $\text{Ni}^{2+}$  ion in its ground-state configuration ( $t_{1g}^3 t_{2g}^3 e_g^2$ ), in the ionic model, become antibonding orbitals in covalent theory. These orbitals are shown schematically in Fig. 1. Also included are the bonding orbitals, which are formed predominantly from ligand  $2s$  and  $2p$  functions. Since their energy is lower than that of the antibonding orbitals, they are completely occupied. According to S&S, it is the covalency of the antibonding electrons which must be considered in order for the experimental observables to be reproduced. Thus, in the theory of the transferred hyperfine effects only the covalency of (spin) unpaired antibonding  $3d$  electrons of majority spin contribute, while the crystal field splitting is associated with the  $3d$  antibonding electrons of minority spin. Sugano and Shulman utilized the conventional approach of treating electrons of either spin identically and therefore obtained a common estimate of this covalent mixing for the two phenomena. In this approach, the bonding electrons are considered to play no role (other than to provide orthogonal partners for the antibonding electrons).

In this paper, the theory of covalency in crystal field phenomena is examined using the cluster model for  $\text{KNiF}_3$  as example. We find the covalent mixing of those *bonding* electrons which have no antibonding partners, to be the appropriate manifestation of covalency in experiment. Unlike the antibonding version described above, it is the covalent mixing of the same (unpaired bonding) electrons (of minority spin in  $\text{KNiF}_3$ ) which contributes to both  $10 Dq$  and the

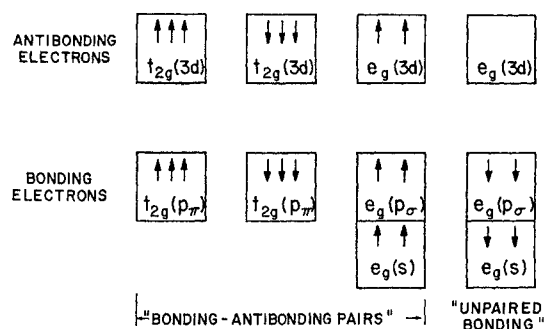


FIG. 1. A schematic representation of the antibonding and bonding electrons grouped into bonding-antibonding pairs and unpaired bonding electrons. For each, the predominant atomic orbital, from which the molecular orbital is formed, is indicated in parentheses; the  $\text{F}^-$  ligand  $2s$ ,  $2p_\sigma$ , and  $2p_\pi$  orbitals are denoted simply by  $s$ ,  $p_\sigma$ , and  $p_\pi$ .

transferred hyperfine interactions and, in fact, to all experimental observables. The covalency (but not the overlap) of the antibonding electrons is entirely irrelevant because it is exactly compensated by the covalency of their bonding partners. This agrees with several features of the role of bonding electrons in transferred hyperfine theory which have been described in the context of the Heitler-London method by Keffer *et al.*<sup>13</sup> and for the molecular orbital (MO) method by Clogston *et al.*<sup>15</sup> These matters are important for if we solve the Hartree-Fock equations for the two types of covalent mixing we find them to differ markedly. This difference does not imply different orbitals for different spin in the sense of unrestricted Hartree-Fock (UHF) theory, because the antibonding covalency (which has *no* physical or variational meaning) may have any value—including that appropriate to the unpaired bonding electrons. (We briefly discuss, for the case of  $\text{Cr}^{3+}$ , the implications of "UHF covalent mixing.")

Two basic aspects of this crystal field theory are considered in what follows: (1) the quantitative implications of the approximations made in the treatment of a Hamiltonian, its matrix elements and related matters; (2) the source and nature of the covalent and overlap effects appropriate to the various physical phenomena. We concentrate on the latter in some detail in the present investigation and leave some aspects of the quantitative calculations to a future paper. Our studies of covalency are described in terms of the occupied one-electron orbitals of the cluster. An alternate approach to crystal field problems consists of dealing with the unoccupied antibonding orbitals, i.e., the antibonding holes (which are associated with the unpaired bonding electrons). Such a treatment of covalent mixing, and the resulting estimates of  $10 Dq$  and other experimental parameters, is exactly equivalent to that associated with the unpaired bonding orbital treatment provided that certain restrictions (to be discussed later) are maintained. For this reason, we will consider only one approach in detail but will make

<sup>11</sup> K. Knox, R. G. Shulman, and S. Sugano, *Phys. Rev.* **130**, 512 (1963); denoted as K, S&S II. R. G. Shulman and S. Sugano, *ibid.* **130**, 506 (1963); denoted as S&S I. R. G. Shulman and K. Knox, *ibid.* **119**, 94 (1960) [in particular, see the discussion between Eqs. (1) and (4)].

<sup>12</sup> See, e.g., P. W. Anderson, *Solid State Phys.* **14**, 99 (1963); of the references cited therein, see, in particular, J. Kondo, *Progr. Theoret. Phys. (Kyoto)* **18**, 541 (1957).

<sup>13</sup> F. Keffer, T. Oguchi, W. O'Sullivan, and J. Yamashita, *Phys. Rev.* **115**, 1553 (1959).

<sup>14</sup> M. Tinkham, *Proc. Roy. Soc. (London)* **A236**, 549 (1956).

<sup>15</sup> A. M. Clogston, T. P. Gordon, V. Jaccarino, M. Peter, and L. R. Walker, *Phys. Rev.* **117**, 1222 (1960).

<sup>16</sup> A. J. Freeman and R. E. Watson, *Phys. Rev. Letters* **6**, 343 (1961).

<sup>17</sup> W. Marshall and R. Stuart, *Phys. Rev.* **123**, 2048 (1961).

brief contact with the unoccupied orbital prediction when describing results.

In Sec. II we describe the covalent mixing of interest to us. A discussion of the one-electron Hamiltonian appropriate to the system follows (in Sec. III). Sections IV and V discuss the covalent mixing appropriate to transferred hyperfine and crystal field splitting effects, respectively. The role of the unpaired bonding electrons becomes apparent in these sections. Throughout, the traditional (and incorrect) antibonding model is examined in parallel. In Sec. VI, we have cause to return to the matter of our Hamiltonian and the crucial role it plays in causing the two types of computed covalent mixing to differ. Since we use an approximate Hamiltonian, as in Ref. 10, certain "self-energy" problems arise which lead to serious internal inconsistencies in the results. The nature of these inconsistencies are explored. Their resolution requires the use of a better approximation to the true one-electron Hamiltonian, a matter reserved for the future. The various matrix elements appearing in our calculations are discussed, and their numerical values are reported, in Sec. VIII. Results, a discussion of their implications for other physical parameters, and conclusions follow.

## II. THE MOLECULAR ORBITAL APPROACH

The molecular orbital approach is by now well known; hence, we will but briefly recapitulate some of the definitions and ideas required by us here. The antibonding molecular orbitals are defined by

$$\begin{aligned}\Psi_e^A &\equiv N_e(\varphi_e - \lambda_s \chi_{2s} - \lambda_\sigma \chi_{2p\sigma}), \\ \Psi_t^A &= N_t(\varphi_t - \lambda_\pi \chi_{2p\pi}),\end{aligned}\quad (1)$$

where the  $N_i$  are normalization constants, the  $\varphi$ 's are  $\text{Ni}^{2+}3d$  orbitals of  $t$  ( $xy$ ,  $yz$ , and  $zx$ ) and  $e$  ( $x^2 - y^2$  and  $3z^2 - r^2$ ) symmetry, and the  $\chi$ 's are appropriate linear combinations<sup>11</sup> of  $2s$ ,  $2p\sigma$ , or  $2p\pi$  atomic orbitals ( $\psi_i$ 's) associated with the six nearest-neighbor  $\text{F}^-$  ions. The  $\lambda_i$ 's are the covalent mixing parameters. The normalization constants are given by

$$\begin{aligned}N_e &= [1 - 2\lambda_s S_s - 2\lambda_\sigma S_\sigma + \lambda_s^2 + \lambda_\sigma^2 + 2\lambda_s \lambda_\sigma S_{s\sigma}]^{-1/2}; \\ N_t &= [1 - 2\lambda_\pi S_\pi + \lambda_\pi^2]^{-1/2},\end{aligned}\quad (2)$$

where an  $S_i$  is the overlap integral between  $\chi_i$  and the  $\varphi_{3d}$  orbital with which it is being combined, and  $S_{s\sigma}$  is the overlap integral between  $\chi_s$  and  $\chi_\sigma$ ; it need not be zero valued, as is often assumed.

One can alternatively speak of the covalent mixing associated with the bonding molecular orbitals,

$$\begin{aligned}\Psi_{es}^B &= N_{es}'(\chi_{2s} + \gamma_s \varphi_e + \gamma_{s\sigma} \chi_{2p\sigma}), \\ \Psi_{e\sigma}^B &= N_{e\sigma}'(\chi_{2p\sigma} + \gamma_\sigma \varphi_e + \gamma_{s\sigma} \chi_{2s}), \\ \Psi_t^B &= N_t'(\chi_{2p\pi} + \gamma_\pi \varphi_t),\end{aligned}\quad (3)$$

where

$$\begin{aligned}N_{es}' &= [1 + 2\gamma_s S_s + 2\lambda_{s\sigma} S_{s\sigma} + 2\gamma_s \gamma_{s\sigma} S_\sigma + \gamma_s^2 + \gamma_{s\sigma}^2]^{-1/2}, \\ N_{e\sigma}' &= [1 + 2\gamma_\sigma S_\sigma + 2\lambda_{s\sigma} S_{s\sigma} + 2\gamma_\sigma \gamma_{s\sigma} S_s \\ &\quad + \gamma_\sigma^2 + \gamma_{s\sigma}^2]^{-1/2}, \\ N_t' &= [1 + 2\gamma_\pi S_\pi + \gamma_\pi^2]^{-1/2}.\end{aligned}\quad (4)$$

The bonding and antibonding orbitals are to be orthonormal, so to lowest order

$$\begin{aligned}\lambda_s &= \gamma_s + S_s, \\ \lambda_\sigma &= \gamma_\sigma + S_\sigma, \\ \lambda_\pi &= \gamma_\pi + S_\pi, \\ \gamma_{s\sigma} &= -\gamma_{s\sigma} - S_{s\sigma}.\end{aligned}\quad (5)$$

The bonding and antibonding orbitals are to be eigenfunctions of the Hartree-Fock (H-F) equations for a  $(\text{Ni}-\text{F}_6)$  cluster in  $\text{KNiF}_6$ , i.e., they are to satisfy

$$h\Psi_i = \epsilon_i \Psi_i, \quad (6)$$

where  $h$  is the one-electron self-consistent H-F Hamiltonian. In the present paper, we will follow Sugano and Shulman and approximate the effects of the crystal external to the cluster by an electrostatic Madelung-like potential  $V_{\text{ext}}$ , i.e., we assume that there are no covalent or overlap effects, between the cluster and its environment, which significantly affect the metal-ligand covalency of interest here. This approximation is necessary in order to make the problem tractable. (One can improve on the approximation by making  $V_{\text{ext}}$  the most accurate description of environmental effects obtainable with a local *effective* potential, but it is well to note that there are shortcomings in such an approach—shortcomings which are particularly significant when one considers superexchange or any other interaction between ions in different clusters.) The use of such a  $V_{\text{ext}}$  is compatible with a self-consistent H-F treatment for the cluster itself.

One automatic result of a self-consistent H-F treatment is that a set of orthonormal one-electron eigenfunctions is obtained. We are thus supplied with a test of the seriousness of any approximation we make in our Hamiltonian (or in evaluating matrix elements) which causes us to fail to have a proper self-consistent theory. The test consists of independently obtaining an antibonding orbital,  $\Psi^A$ , and its bonding partner,  $\Psi^B$ , and checking their orthogonality. We will see that the present approximate cluster theory does not always meet this orthogonality requirement.

We will solve Eq. (6) for  $\Psi$  within a very limited function space, namely, one spanned by the molecular orbitals constructed from  $\text{Ni}^{2+}$  and ligand-free ion orbitals. (One well might wish to allow greater variational freedom in a future calculation.) However, what is important to us here, is that the limited nature of this space in no way effects eigenfunction orthogonality or the self-energy problem to be discussed in Sec. VI. Let us

now consider, in detail, the nature of the one-electron Hamiltonian.

### III. THE ONE-ELECTRON HAMILTONIAN

We are interested in obtaining the exact one-electron H-F Hamiltonian, appropriate to Eq. (6), derived from a many-electron Hamiltonian consisting of kinetic and electrostatic terms, where the environment external to the  $(\text{Ni}-\text{F}_6)$  cluster is approximated by a Madelung-like one-electron electrostatic potential  $V_{\text{ext}}(r_i)$ . The process is made trivial by the fact that the two H-F many-electron states of interest to us are single determinants constructed from orthonormal one-electron orbitals ( $\Psi^A$ 's and  $\Psi^B$ 's). For such states the one-electron Hamiltonian  $h_i$ , for electron orbital  $i$ , is simply

$$h_i(r_1) = \frac{1}{2}\nabla_1^2 + \sum_{\alpha} \left( -\frac{Z_{\alpha}}{r_{\alpha 1}} \right) + V_{\text{ext}}(r_1) + \sum \int \Psi_j^*(r_2) \frac{1-P_{12}}{r_{12}} \Psi_j(r_2) d\tau_2 \quad (7)$$

in atomic units. The  $\alpha$  summation (over nuclear potential contributions) is limited to the one Ni and six F nuclei for we have already introduced the potential accounting for all electrons and nuclei (presumed) external to the cluster. The  $P_{12}$  operator permutes coordinates  $r_1$  and  $r_2$  giving us the interelectronic exchange terms, which occur only between electrons of common spin. The sum over interelectronic terms is limited to the cluster and consists of contributions from all electrons in the cluster including the  $i$ th electron itself. This is allowed in a self-consistent H-F theory because the  $i$ th electron Coulomb contribution is exactly canceled by its exchange term. We will have occasion to return to the matter of including or excluding an electron's self-energy contribution to Eq. (7) later.

We now wish to re-express the interelectronic potential of  $h$  in terms of one-electron functions localized on the seven nuclei in the cluster, for it is in terms of these that the potential, of Eq. (7), can be evaluated. In this simple procedure the  $\Psi$ 's are expressed as linear combinations of the local atomic orbitals (LCAO's), i.e.,  $\Psi$  is broken up into Ni  $\varphi$  and ligand  $\chi_i$  orbitals [with the  $\chi_i$ 's themselves expressed in terms of local orbitals ( $\psi_i$ 's) at the various fluorine sites], whereupon Eq. (7) may be written as

$$h_i(r_1) = -\frac{1}{2}\nabla_1^2 + V_{\text{ext}}(r_1) + V_m(r_1) + V_L(r_1) + V_S^{(1)}(r_1) + V_{\gamma}^{(1)}(r_1) + V_S^{(2)}(r_1) + V_{\gamma}^{(2)}(r_1) + V_{SL}(r_1). \quad (8)$$

As we shall see, the terms of the second line account for the important fact that the local one-electron functions of one center are nonorthogonal with those of another (i.e.,  $S \neq 0$ ) and that there is covalent mixing.

Let us now consider the individual terms separately.  $V_m$ : This term is simply the H-F nuclear and inter-electronic Coulomb plus exchange potential for an isolated  $\text{Ni}^{2+}$  ion;

$$V_m(r_1) = -\frac{Z_{\text{Ni}}}{r_1} + \sum_{\substack{j=\text{all Ni}^{2+} \\ \text{electrons}}} \int \varphi_j^*(r_2) \frac{1-P_{12}}{r_{12}} \varphi_j(r_2) d\tau_2. \quad (9)$$

$V_L$ : These are similar contributions from the ligand ions;

$$V_L(r_1) = \sum_{\alpha=1}^6 \left\{ \frac{-Z_{\alpha}}{r_{1\alpha}} + \sum_{\substack{j=\text{all electrons} \\ \text{on ion } \alpha}} \int \psi_{j,\alpha}^*(r_2) \frac{1-P_{12}}{r_{12}} \times \psi_{j,\alpha}(r_2) d\tau_2 \right\}. \quad (10)$$

The above terms would make up the interelectronic contributions coming from the cluster if there were neither covalent mixing *nor* any overlap between orbitals on different sites. The omission of overlap terms may be thought of as yielding a potential of the form one would have when the ions of the cluster are infinitely separated. It is important to note that such a potential [actually the full first line of Eq. (8)] was used by Sugano and Shulman in their work. The consequences of this approximation will be discussed later.

Next we consider the overlap contributions to the potential.  $V_S^{(1)}(r_1)$  and  $V_S^{(2)}(r_1)$ : The most obvious overlap effects are associated with metal-ligand non-orthogonality. In the case of zero covalency, this nonorthogonality is resolved by having  $\lambda_i = S_i$  while  $\gamma_i = 0$  for the bonding-antibonding pairs. Setting  $\lambda_i$  and  $\gamma_i$  to these values, we can inspect the overlap terms arising in Eq. (8). There are terms linear in  $S$ , i.e.,

$$V_S^{(1)}(r_1) = -\sum_j 2S_j \int \varphi_j^*(r_2) \frac{1-P_{12}}{r_{12}} \chi_j(r_2) d\tau_2, \quad (11)$$

where the sum is over all bonding-antibonding pairs. Note that Eq. (11) is written in terms of the multicenter ligand molecular orbitals,  $\chi_j$ . There are also higher order overlap terms in  $S_j$ , i.e.,

$$V_S^{(2)}(r_1) = +\sum_j S_j^2 \left\{ \int \varphi_j^*(r_2) \frac{1-P_{12}}{r_{12}} \varphi_j(r_2) d\tau_2 + \int \chi_j^*(r_2) \frac{1-P_{12}}{r_{12}} \chi_j(r_2) d\tau_2 \right\} + O(S^3). \quad (12)$$

These second-order terms are of the same order of importance as  $V_S^{(1)}$  which involves an  $S_j$  times an overlap charge density. Note that a  $\varphi_e$  appears twice in the summations in these equations to account for its two partners,  $\chi_e$  and  $\chi_{e'}$ . Third and higher order terms are, of course, less important.

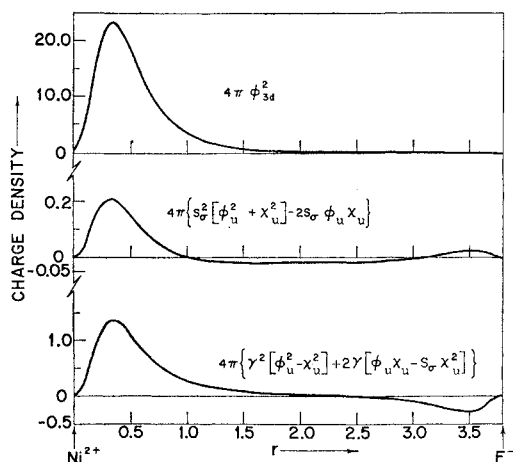


FIG. 2. The charge density of  $4\pi\varphi_u^2$  of the  $u(=3z^2-r^2)$  orbital compared with the  $p$  electron overlap charge density  $4\pi\{S_u^2[\varphi_u^2+X_u^2]-2S_u\varphi_u X_u\}$  and covalent charge density  $4\pi\{\gamma^2[\varphi_u^2-X_u^2]+2[\varphi_u X_u-S_u X_u^2]\}$  plotted along the  $z$  axis from  $\text{Ni}^{2+}$  to  $\text{F}^-$ . Densities are all in the same units, normalized such that  $\int \varphi_{3d}^2(\mathbf{r})d\tau=1$ ; the free ion  $S$  value was used (see Table VII) and  $S+\gamma$  was chosen so as to reproduce the experimental (Ref. 11) anisotropic  $\text{F}^-$  hyperfine term.

In Fig. 2 we plot the overlap charge density, giving rise to the sum of the  $V_S^{(1)}$  and  $V_S^{(2)}$  terms, along a metal-ligand axis, and for comparison, the charge density associated with an antibonding electron prior to the introduction of overlap and covalency [i.e., just  $|\varphi_i(\mathbf{r})|^2$ ]. We see that the antibonding charge density has been delocalized, by the addition of the overlap terms, in the sense that there has been a buildup of charge on the ligand (which is one of six so affected), but, there has also been an increase of charge on the metal as well. These increases have been compensated for by a decrease of charge due to the  $-2S_i[\varphi_i^*(\mathbf{r})X_i(\mathbf{r})]$  term, in the region between the ions. In other words, one is not dealing with a shift in charge (or spin) simply from one ion to another but onto the ions from the region between. The often cited picture of overlap (and covalent) effects delocalizing charge and spin off the metal ion is, therefore, not valid, for we are dealing with a process which is more complicated. Whether the overlap effect *acts as if* there is a shift onto, or off, the metal ion, depends strongly on the nature of the operator whose expectation value is in question.

$V_{SL}$ : These are additional overlap potential contributions due to the nonorthogonality between ligand orbitals. First, ligand-ligand ( $\psi-\psi$ ) overlap enters into the evaluation of the second line of Eq. (12) (where we have  $X^2$ ), and elsewhere. We will include the latter terms as part of  $V_{SL}$  but will not write them out explicitly. It should be noted that the normalization of the  $X_i$ 's as defined in S&S I [Eq. (2.4)], is affected by this nonorthogonality; however, for the purposes of this paper, we assume their normalization convention. Secondly,  $X_s-X_\sigma$  nonorthogonality leads to additional potential terms, the lowest order ones being of the

form

$$S_{ss}^2 \left[ \int \chi_\sigma^*(r_2) \frac{1-P_{12}}{r_{12}} \chi_\sigma(r_2) d\tau_2 + \int \chi_s^*(r_2) \frac{1-P_{12}}{r_{12}} \chi_s(r_2) \right] - 2S_{ss} \int \chi_\sigma^*(r_2) \frac{1-P_{12}}{r_{12}} \chi_s(r_2) d\tau_2 \quad (13)$$

similar to what we have seen in Eqs. (11) and (12). Finally, the simultaneous nonorthogonality of  $\varphi_e$  with  $X_s$  and  $X_\sigma$ , which leads to terms involving the  $X_\sigma X_s$  charge density, have been arbitrarily included in  $V_{SL}$ . The lowest order term is of the form

$$2S_s S_\sigma \int \chi_s^*(r_2) \frac{1-P_{12}}{r_{12}} \chi_\sigma(r_2) d\tau_2 \quad (14)$$

and is of higher order than the contributions written out explicitly in Eqs. (11), (12), and (13), i.e., it is the product of two overlap integrals times an overlap charge density potential. Finally we come to covalent contributions.  $V_\gamma^{(1)}(r_1)$ ,  $V_\gamma^{(2)}(r_2)$ : These are most simply obtained by evaluating the interelectronic term Eq. (8) for nonzero  $\gamma_j$  (with  $\lambda_j=\gamma_j+S_j$ ), and subtracting off the overlap terms already accounted for in  $V_S^{(1)}$  and  $V_S^{(2)}$ . One obtains linear terms of the form

$$V_\gamma^{(1)}(r_1) = - \sum_{j=\text{antibonding orbitals}} 2\gamma_j \int \varphi_j^*(r_2) \frac{1-P_{12}}{r_{12}} \chi_j(r_2) d\tau_2 + \sum_{j=\text{bonding orbitals}} 2\gamma_j \int \varphi_j^*(r_2) \frac{1-P_{12}}{r_{12}} \chi_j(r_2) d\tau_2. \quad (15)$$

It is immediately apparent that contributions from members of an occupied bonding-antibonding pair cancel one another, leaving us *only* with contributions coming from *unpaired bonding orbitals*, i.e.,

$$V_\gamma^{(1)}(r_1) = + \sum_{j=\text{unpaired bonding orbitals}} 2\gamma_j \int \varphi_j^*(r_2) \frac{1-P_{12}}{r_{12}} \times \chi_j(r_2) d\tau_2. \quad (16)$$

Such cancellations also occur for the covalent mixing involving (a nonzero)  $\gamma_{ss}$  in a  $\Psi_s^B-\Psi_\sigma^B$  pair. A similar cancellation occurs in second order giving us

$$V_\gamma^{(2)}(r_1) = + \sum_{j=\text{unpaired bonding}} \left\{ \gamma_j^2 \left[ \int \varphi_j^*(r_2) \frac{1-P_{12}}{r_{12}} \varphi_j(r_2) d\tau_2 - \int \chi_j^*(r_2) \frac{1-P_{12}}{r_{12}} \chi_j(r_2) d\tau_2 \right] - 2\gamma_j S_j \int \chi_j^*(r_2) \frac{1-P_{12}}{r_{12}} \chi_j(r_2) d\tau_2 \right\} + \text{higher order terms.} \quad (17)$$

The cancellation illustrated in detail above follows simply from a well-known property of determinantal functions: Any linear combination of occupied orbitals in a Slater determinant leaves unchanged the expectation value of an operator—and hence does not affect the prediction of any physical observable.

The first line of Eq. (17) is associated with an obvious physical effect, namely, the transfer of charge from ligand to metal ions due to covalent mixing. The number of electrons so transferred is simply

$$N = \sum_{j=\text{unpaired bonding orbitals}} \gamma_j^2. \quad (18)$$

Antibonding-bonding pairs do not contribute to this transfer because the covalency of one is compensated for by that of the other, as is required, to second order, by the orthogonality conditions [Eqs. (5)]. The third line of Eq. (17) is coupled with  $V_\gamma^{(1)}$  which is  $2\gamma_j$  times an overlap potential. The two terms represent a first-order (in  $\gamma_j$ ) shift of charge off the ligands into the space between ligands and the Ni<sup>2+</sup> ion. It should be noted that as the unpaired bonding orbitals are of minority spin, the covalent terms involve a shift of minority spin onto the metal ion, effectively reducing the net spin localized at the Ni<sup>2+</sup> site. These covalent charge density terms are plotted for a bonding  $2p\sigma$  electron in Fig. 2 (their negative should be taken when considering spin effects) where  $\gamma$  was chosen so as to reproduce the experimental<sup>11</sup> anisotropic transferred hyperfine interaction. This choice causes these covalent effects to be greater than the overlap terms for the same  $e_g$  electrons. Such a dominance need not always occur. Note that there are also  $t_{2g}$  and Ni closed shell overlap charge, but *not* spin, density effects. The overlap and covalent  $e_g$  terms act cooperatively in their contributions to the Ni<sup>2+</sup> charge and F<sup>-</sup> spin densities while making opposing contributions to the Ni<sup>2+</sup> spin and F<sup>-</sup> charge behaviors.

We have seen a covalent shift of charge associated with unpaired bonding electrons and no such shift for bonding-antibonding pairs. This fact is of great interest to us for reasons beyond the mere matter of estimating a potential, for it indicates the profoundly different nature of the two types of covalent mixing. The mixing of a bonding-antibonding pair conserves the charge on the metal ion while that of an unpaired bonding electron involves the shift of charge from ligands to metal. This observation suggests that the computed covalent mixing, i.e., the  $\gamma_i$ , differs for the two cases and is the reason for our preoccupation with bonding electron behavior in this paper.

In the above discussion of the overlap and covalent contributions to the Hamiltonian,  $h$ , we deliberately neglected to specify exactly which orbitals were so involved. As covalent terms only occur in low order for unpaired bonding orbitals we need only consider those electrons which can enter into bonding with the open  $3d$  shell; i.e., the  $2s$ ,  $2p$ , and  $1s$  shells of the ligands.

The  $2s$  and  $2p$  electrons are expected to make small contributions, and the  $1s$  electrons insignificant contributions, to  $V_\gamma^{(1)}$  and  $V_\gamma^{(2)}$ .

We also expect the overlap terms to make a more significant contribution to the potential terms than do the covalent terms. Now, any shell which significantly overlaps another ion shell should be included in  $V_S^{(1)}$ ,  $V_S^{(2)}$ , and/or  $V_{SL}$ . Hence, when including overlap terms in the potential one must inspect terms other than the Ni  $3d$  and ligand  $2s$  and  $2p$  electrons, to which consideration is normally limited. In particular, one should, at the minimum, explore the role of the Ni  $3s$  and  $3p$  shells since their overlap with the ligand electrons is only moderately smaller than that of the  $3d$  orbitals.

In the present paper we will follow the Sugano and Shulman treatment and mostly limit ourselves to a Hamiltonian (denoted by  $h_0$ ) consisting of the first line of Eq. (8) alone for two reasons. First, we believe it imperative to fully explore the implications of their approximations, approximations which at first glance seem to yield excellent agreement with experiment, before going on to a more complete (and more complicated) treatment. Secondly, a more complete treatment appears to require far greater care in the numerical evaluation of matrix elements than does a treatment based on  $h_0$  alone. Greater care is not only necessary in the handling of overlap and covalent terms but also in the evaluation of the  $h_0$  matrix elements. Approximations which were apparently adequate for the simple case must be re-examined before one attempts the more detailed treatment; this is due, in part, to the severe numerical differencing which occurs in the course of evaluating matrix elements. Our reasons for being cautious on this matter will become obvious when we inspect the results of the present paper.

As Sugano and Shulman have emphasized, the use of  $h_0$  can be viewed as the first iteration of a self-consistent theory for the (Ni—F<sub>6</sub>) covalent mixing problem. This is so, providing that overlap as well as covalent terms are included in a later iteration. As we shall see, the results of Sec. VIII suggest that a proper evaluation of covalent effects cannot be had without the inclusion of the overlap and covalent terms in the Hamiltonian [i.e., the second line of Eq. (8)]. It is our intention to investigate the effect of such terms in a future paper.

In going beyond the use of  $h_0$ , one is involved in an ever increasing commitment to details of the cluster model, details which do not reflect the situation in the actual crystal. The use of  $h_0$  and the MO's as defined earlier for the cluster already imply a strong commitment.

#### IV. UNPAIRED SPIN COVALENCY AND TRANSFERRED HYPERFINE EFFECTS

We now consider the role of covalent mixing in transferred hyperfine effects. In doing this, we assume that the orthogonality relations of Eq. (5) hold and

that orbitals differing in spin may have different covalent parameters.

The isotropic  $F^{19}$  hyperfine parameter is considered to be primarily associated<sup>14,11</sup> with the unpaired  $2s$  spin induced by nonorthogonality and covalency on the  $F^-$  site. After a variety of other contributions<sup>16,17,11</sup> are accounted for, the parameter is written as the product of the hyperfine constant associated with a single  $F^- 2s$  orbital times the fraction,  $f_s$ , of induced unpaired  $2s$  spin character at the  $F^-$  site. Making the standard assumption of constant covalency for electrons of either spin, the value of  $f_s$  in  $\text{KNiF}_3$  is

$$f_s = \lambda_e^2 N_e^2 / 3 \quad (19)$$

and arises from the antibonding electrons alone. The  $\frac{1}{3}$  accounts for the fact that  $\lambda$  is defined in terms of molecular orbitals and that we are interested in the  $2s$  character induced on a single  $F^-$  site (via both antibonding  $e_\uparrow$  orbitals). The anisotropic hyperfine interaction is complicated by the presence of (1) both  $p_\sigma$  and  $p_\pi$  contributions and (2) a substantial correction for classical spin dipolar effects (which must be made prior to estimating covalency from experiment). The  $p$ -electron interaction is entirely spin dipolar (i.e., not orbital) and given the experimental covalent hyperfine parameter, the fractional difference ( $f_\sigma - f_\pi$ ) between induced  $p_\sigma$  and  $p_\pi$  behavior can be inferred.

The conventional assumption of common covalency for either spin leads to  $f_\pi = 0$  for  $\text{KNiF}_3$  since all  $t$  orbitals are occupied in the ground state. Experiment, therefore, would seem to yield information concerning the  $2s$  and  $2p_\sigma$  covalent mixing in the antibonding  $e_\uparrow$  orbitals from the observed isotropic and anisotropic interactions.

The above discussion assumes that the transferred hyperfine interaction is entirely due to the spin density associated with a ligand's  $\psi$  orbitals. However, the tails of the free ion  $\text{Ni } \varphi_{3d}$  (and neighboring ligand) orbitals overlap into the region of a F nucleus and contribute<sup>16,17</sup> to the spin density and hyperfine interaction via the  $\varphi^2$  and  $\varphi\chi$  terms. These terms are not negligible.<sup>16</sup> Unfortunately the use of free ion orbitals is inappropriate for this evaluation since these orbitals do not take account of the presence of neighboring ion nuclei. We will encounter similar problems, introduced by inappropriate orbital tail behavior, when discussing orbital reduction effects in Sec. IX. These matters will be ignored in the remainder of this section.

Let us now consider how the picture changes when one accounts for all covalent mixing while maintaining the necessary orthogonality of bonding and antibonding orbitals to second order in  $S_i$ ,  $\chi_i$ , and  $\gamma_i$ . We will again consider the  $2s$  effects as they are the least complicated. The implications for anisotropic effects will then be immediately apparent.

Consider the contributions to  $f_s$  from the bonding  $e_\uparrow$  and  $e_\downarrow$ , and antibonding  $e_\uparrow$  electrons. Writing out the

normalization constant in Eq. (17) and making use of Eq. (5), the antibonding contribution becomes

$$f_{s\uparrow}^A = \frac{1}{3} \{ S_s^2 + 2S_e \gamma_{s\uparrow} + \gamma_{s\uparrow}^2 \} + 0(S^3). \quad (20)$$

(We will henceforth use superscripts  $A$  and  $B$  to denote antibonding and bonding, respectively, whenever appropriate for clarity.) In the absence of covalent bonding and  $\chi_e - \chi_\sigma$  overlap, the  $f_s$  contributions are  $+1$  for spin  $\uparrow$  and  $-1$  for spin  $\downarrow$ , and hence cancel. Covalency affects these  $f_s$  contributions via (1) the normalization of the  $\Psi_{e_s^B}$  orbitals [cf. Eq. (4)] and (2) the  $\chi_{2s}$  term of  $\Psi_{e_s^B}$ . With differing covalency, these contributions need no longer cancel. The individual spin contributions are

$$f_{s\uparrow}^B = \frac{1}{3} N_{s\uparrow}^2 + \frac{1}{3} N_{\sigma\uparrow}^2 \gamma_{\sigma s\uparrow}^2 \\ = \frac{1}{3} \{ 1 - 2\gamma_{s\uparrow} S_e - \gamma_{s\uparrow}^2 + S_{e\sigma}^2 \} + 0(S^3) + \dots, \quad (21)$$

$$f_{s\downarrow}^B = -\frac{1}{3} \{ 1 - 2\gamma_{s\downarrow} S_e - \gamma_{s\downarrow}^2 + S_{e\sigma}^2 \} + 0(S^3) + \dots \quad (22)$$

Combining all these contributions results in

$$f_s = \frac{1}{3} \{ S_e^2 + 2\gamma_{s\downarrow} S_e + \gamma_{s\downarrow}^2 \} + 0(S^3). \quad (23)$$

Similarly, one obtains

$$f_s = \frac{1}{3} \{ S_e^2 + 2S_e \gamma_{\sigma s\downarrow} + \gamma_{\sigma s\downarrow}^2 \} + 0(S^3). \quad (24)$$

In other words, if bonding and antibonding orbitals of one spin are simultaneously occupied, there will be an  $S_e^2$  overlap contribution, but their covalent terms cancel exactly. Hence, it is the covalency of the *bonding*  $e_{s\downarrow}^B$  electrons which contribute to the isotropic transferred hyperfine interaction in  $\text{KNiF}_3$ , and if there is any question as to the constancy of  $2s$  covalent mixing within the set of  $e$  orbitals, it is the mixing estimated for the  $e_{\downarrow}^B$  electrons which must be compared with experiment.

The conventional cancellation associated with spin pairing has been lost, but the more fundamental pairing cancellation between bonding and antibonding orbitals has been seen. The immediate effects of this for the anisotropic  $F^-$  hyperfine interaction are (1) that  $t_\uparrow$  and  $t_\downarrow$  electrons cannot contribute, no matter what their respective covalencies, since antibonding-bonding pairs of both spins are occupied; (2) that there will be  $S^2$ , but no  $\gamma$  contributions from the majority spin  $e_\uparrow^B$  and  $e_\uparrow^A$  electrons; and (3) that covalent contributions come solely from unpaired  $e_{\downarrow}^B$  electrons of minority spin. It is clear from the identical form of Eqs. (20) and (23) that the usual phenomenological approach, which uses the antibonding expression [Eq. (20)], actually determines<sup>15</sup> the unpaired bonding covalent mixing parameter.

Complications occur for almost empty  $d$  shell ions such as  $\text{Cr}^{3+}(t_1^A)^3$  which has but three antibonding  $d$ -like electrons. There are no  $e^A$  electrons in the ground state and differences in  $e_\uparrow^B$  and  $e_\downarrow^B$  covalent mixing can lead, for example, to an isotropic  $F^-$  hyperfine term which would be zero in the traditional analysis.

Transferred hyperfine effects have been observed<sup>18</sup> in K<sub>2</sub>NaCrF<sub>6</sub>; the isotropic term is almost zero valued. This either implies that the  $e^B$  covalency differences are very small here or that an accidental near cancellation of a number of contributions has occurred. Neutron diffraction experiments on such a system could test for  $e$  electron character in the cluster's spin density.

It must be stressed that any computed differences in  $e^B - e^A$  covalency, for this case, come from a different source than do the differences between the covalency of an occupied Ni<sup>2+</sup> bonding-antibonding pair of one spin and that of an unpaired bonding orbital of the other. The covalent "unpairing" of the Cr<sup>3+</sup> orbitals has its source in the unbalanced exchange terms of the open  $3d$  shell. By this we do not mean the HF exchange polarization of the F<sup>-</sup> ion by the  $3d$  shell, a matter discussed elsewhere.<sup>19</sup> Instead, we mean the imbalance in covalent mixing caused by the imbalance in  $3d$  exchange contributions to  $h_0$  and, in turn, the various matrix elements appropriate to the determination of the covalent mixing. Although these exchange terms also contribute to the Ni<sup>2+</sup> case, a more fundamental role is played by the intrinsic differences in the character of the antibonding-bonding pair covalency, on the one hand, and that of the unpaired bonding electrons on the other. Note that the unbalanced exchange terms cause the single determinant description of the Cr<sup>3+</sup> cluster to be an improper eigenfunction, and of the Ni<sup>2+</sup> cluster, to be a proper eigenfunction, of the spin operator ( $S^2$ ). The Ni<sup>2+</sup> description preserves its symmetry because of the presence of unpaired bonding orbitals of but one spin.<sup>20</sup>

## V. THE CRYSTAL FIELD SPLITTING

We use the conventional definition of the crystal field splitting, namely,

$$10 Dq \equiv \mathcal{E}[(t^{EA})^5(e^{EA})^3] - \mathcal{E}[(t^A)^6(e^A)^2], \quad (25)$$

where the latter is the energy of the ground state and the former is the energy of the excited state (hence the superscript  $E$  to designate this state) obtained by replacing the  $t(xy)_\downarrow^A$  electron of the ground state by an  $e(x^2-y^2)_\downarrow^A$  electron. If we make the common, but often unjustified,<sup>21</sup> assumption that all electrons but the promoted one maintain constant orbital behavior in the cluster states, we have

$$10 Dq = \epsilon[e(x^2-y^2)_\downarrow^{EA}] - \epsilon[t(xy)_\downarrow^A], \quad (26)$$

where the  $\epsilon$ 's are the eigenvalues obtained with Eq. (6) for the one-electron Hamiltonian appropriate to the

<sup>18</sup> R. G. Shulman and K. Knox, Phys. Rev. Letters 4, 603 (1960).

<sup>19</sup> A. J. Freeman and R. E. Watson, J. Appl. Phys. 34, 1032S (1963); and (to be published).

<sup>20</sup> This observation is subject to the restriction that the  $\Psi$ 's be constructed from a set of free ion  $\varphi$ 's and  $\psi$ 's having a single radial function per shell (although different  $\varphi_e$  and  $\varphi_t$  radial behavior is allowed).

<sup>21</sup> For example see, R. E. Watson, Phys. Rev. 118, 1036 (1960); in particular Tables V-VIII and related text.

particular cluster state involved. To second order,

$$\epsilon_t^A = \langle \varphi_t | h | \varphi_t \rangle - 2S_t \langle \varphi_t | h | \chi_t \rangle - 2\gamma_t \langle \varphi_t | h | \chi_t \rangle + \{ [S_t + \gamma_t]^2 \langle \chi_t | h | \chi_t \rangle + [S_t^2 - \gamma_t^2] \langle \varphi_t | h | \varphi_t \rangle \}, \quad (27)$$

which is obtained by multiplying Eq. (6) from the left by  $\Psi$ , reexpressing the  $\Psi$ 's in terms of  $\varphi$ 's and  $\chi$ 's, integrating and keeping all terms to second order. The first term of  $\epsilon$  is simply the diagonal energy and includes the classic point charge crystal potential, Kleiner's correction<sup>5</sup> to such a potential, and ligand exchange terms; the second term is the first-order contribution to the overlap energy of the sort investigated by Tanabe and Sugano<sup>7</sup>; we then have the first-order term of the covalent contribution, which Sugano and Shulman concluded was important; and lastly, the second-order terms in overlap and covalency. The expression for  $\epsilon_e^A$  is of the form of Eq. (27) except that there are first- and second-order overlap and covalent contributions from both the  $\chi_s$  and  $\chi_\sigma$  mixing, i.e.,

$$\epsilon_e^A = \langle \varphi_e | h | \varphi_e \rangle - \sum_{i=s,\sigma} \{ 2(S_i + \gamma_i) \langle \varphi_e | h | \chi_i \rangle + [S_i + \gamma_i]^2 \times \langle \chi_i | h | \chi_i \rangle + [S_i^2 - \gamma_i^2] \langle \varphi_e | h | \varphi_e \rangle \}. \quad (28)$$

One may obtain alternative expressions<sup>10</sup> for the  $\epsilon$ 's, for example, by multiplying Eq. (16) by  $\chi$  instead of  $\Psi$ , in which case  $\epsilon^A$  is given by

$$\epsilon_t^A = \langle \varphi_t | h | \varphi_t \rangle - (S_t + \gamma_t) \langle \varphi_t | h | \chi_t \rangle + S_t(S_t + \gamma_t) \langle \varphi_t | h | \varphi_t \rangle. \quad (29)$$

Note the omission of the two multiplying the linear term.<sup>22</sup> Unlike Eq. (27), this relation only holds if  $\Psi$  is an eigenfunction of Eq. (6) (within our  $\varphi, \chi$  subspace), in which case Eqs. (27) and (29) differ from one another in third and higher order in  $S$  and  $\gamma$ . This point is of some importance for we shall be evaluating Eq. (25) [and thus Eq. (27)] using noncovalent orbitals ( $\gamma=0$ ).

We have already seen indications that the computed covalent mixing appropriate to a bonding-antibonding pair differs from that of an unpaired bonding electron. This suggests that the covalent mixing of the paired  $t(xy)_\downarrow^B$  [and unpaired  $e(x^2-y^2)_\downarrow^B$ ] orbital [ $s$ ], appearing in the ground state, might very well undergo substantial changes on becoming an unpaired (and paired) electron in the excited state. We must then inspect the role of bonding orbital crystal field energies. The one-electron energy of a bonding  $t$  electron is, for example,

$$\epsilon_t^B = \langle \chi_t | h | \chi_t \rangle + 2\gamma_t \langle \varphi | h | \chi_t \rangle + \{ \gamma_t^2 \langle \varphi | h | \varphi \rangle - (2\gamma_t S_t + \gamma_t^2) \langle \chi_t | h | \chi_t \rangle \}. \quad (30)$$

<sup>22</sup> Their counterpart of the second line [e.g., in S&S III, Eq. (2.11)] shows a  $\langle \varphi_e | h_0 | \varphi_e \rangle$  matrix element but we find  $\langle \varphi_t | h_0 | \varphi_t \rangle$  more appropriate for this case.



The energy of a bonding-antibonding  $t$  orbital pair,  $\Omega_t$ , in a crystal field is then

$$\begin{aligned} \Omega_t &= \epsilon_t^B + \epsilon_t^A - \langle \Psi_t^A \Psi_t^A | \Psi_t^B \Psi_t^B \rangle + \langle \Psi_t^A \Psi_t^B | \Psi_t^A \Psi_t^B \rangle \\ &= -S_t \langle \chi_t | h | \varphi_t \rangle + (1 + S^2) \{ \langle \varphi_t | h | \varphi_t \rangle + \langle \chi_t | h | \chi_t \rangle \\ &\quad - \langle \varphi_t \varphi_t | \chi_t \chi_t \rangle + \langle \varphi_t \chi_t | \varphi_t \chi_t \rangle \}, \quad (31) \end{aligned}$$

where

$$\begin{aligned} &\langle \Psi_A \Psi_B | \Psi_C \Psi_D \rangle \\ &\equiv \iint d\tau_1 d\tau_2 \Psi_A^*(\mathbf{r}_1) \Psi_B(\mathbf{r}_1) \frac{1}{r_{12}} \Psi_C(\mathbf{r}_2) \Psi_D^*(\mathbf{r}_2). \quad (32) \end{aligned}$$

The two-electron terms of the first line of (31) account for the fact that the interelectronic interaction between the pair of electrons has been counted twice when summing  $\epsilon^B$  plus  $\epsilon^A$ . An equivalent expression is obtainable for the  $e$  bonding electron; its derivation is but slightly complicated by the simultaneous presence of  $s$  and  $\sigma$  mixing.

In Eq. (31) as in Eqs. (16) and (17) we see the effect of the antibonding-bonding cancellation. The covalency of a bonding-antibonding pair plays no role in the cluster's energy<sup>15</sup> and hence in the crystal field splitting. Of course these pairs still make diagonal and overlap contributions to both the crystal field energy and to the Hamiltonian.

It is clear that only the unpaired bonding electrons make covalent contributions to the energies of Eq. (25). These total energies ( $\mathcal{E}$ ) can be evaluated by a simple summation over one-electron  $\epsilon$ 's, providing that we account for the fact that this procedure introduces each interelectronic interaction twice by subtracting interelectronic Coulomb and exchange terms [as we did in Eq. (31)]. Here, we wish to concentrate on those  $\epsilon$ 's which contribute to a nonzero  $10Dq$ , namely all unpaired bonding electrons (which contribute covalent terms) and the bonding-antibonding pairs involved in the transition (which make diagonal and overlap contributions). The resulting  $\mathcal{E}$ 's are

$$\mathcal{E}[(t^A)^0(e^A)^2] = \epsilon_{xy\downarrow}^A + \epsilon_{xy\downarrow}^B + \epsilon_{s,v\downarrow}^B + \epsilon_{s,u\downarrow}^B + \epsilon_{\sigma,v\downarrow}^B + \epsilon_{\sigma,u\downarrow}^B + \sum_{i>j} [\langle \Psi_i \Psi_j | \Psi_j \Psi_i \rangle - \langle \Psi_i \Psi_j | \Psi_i \Psi_j \rangle] + \mathcal{E}_c \quad (33)$$

and

$$\mathcal{E}[(t^E)^0(e^E)^2] = \epsilon_{v\downarrow}^E + \epsilon_{s,v\downarrow}^E + \epsilon_{\sigma,v\downarrow}^E + \epsilon_{xy\downarrow}^E + \epsilon_{s,u\downarrow}^E + \epsilon_{\sigma,u\downarrow}^E + \sum_{i>j} [\langle \Psi_i \Psi_j | \Psi_j \Psi_i \rangle - \langle \Psi_i \Psi_j | \Psi_i \Psi_j \rangle] + \mathcal{E}_c, \quad (34)$$

where  $\mathcal{E}_c$  is common to both energies and the sums go over all pairs of orbitals represented by the  $\epsilon$ 's. The subscripts  $v$  and  $u$  designate the  $(x^2 - y^2)$  and  $(3z^2 - r^2)$  orbitals of  $e$  symmetry, respectively. The  $v$  orbital is involved in the crystal field transition ( $t_{xy}^A \rightarrow e_{x^2 - y^2}^A$ ) and the  $u$  orbitals are the "odd" unpaired bonding orbitals common to both crystal field states. Evaluating Eq. (25), rearranging terms and affecting appropriate cancellations, we have,

$$\begin{aligned} 10Dq &= \{ \langle \phi_e | h^E - V_{xy} \gamma^E - V_{s,u} \gamma^E - V_{\sigma,u} \gamma^E | \phi_e \rangle - \langle \phi_t | h - V_{s,v} \gamma - V_{\sigma,v} \gamma - V_{s,u} \gamma - V_{\sigma,u} \gamma | \phi_t \rangle \} \\ &+ \sum_{\substack{i=s, j=\sigma \\ i=\sigma, j=s}} \{ S_i^2 [\langle \chi_{i,v} | h^E - V_{xy} \gamma^E - V_{s,u} \gamma^E - V_{\sigma,u} \gamma^E - \frac{1}{2} V_{j,v} S | \chi_{i,v} \rangle + \langle \phi_v | h^E - V_{xy} \gamma^E - V_{s,u} \gamma^E - V_{\sigma,u} \gamma^E - \frac{1}{2} V_{j,v} S | \phi_v \rangle] \\ &- 2S_i \langle \chi_{i,v} | h^E - V_{xy} \gamma^E - V_{s,u} \gamma^E - V_{\sigma,u} \gamma^E - \frac{1}{2} V_{j,v} S | \phi_v \rangle \} - \{ S_\pi^2 [\langle \chi_\pi | h - V_{s,v} \gamma - V_{\sigma,v} \gamma - V_{s,u} \gamma - V_{\sigma,u} \gamma | \chi_\pi \rangle \\ &+ \langle \phi_{xy} | h - V_{s,v} \gamma - V_{\sigma,v} \gamma - V_{s,u} \gamma - V_{\sigma,u} \gamma | \phi_{xy} \rangle] - 2S_\pi \langle \chi_\pi | h - V_{s,v} \gamma - V_{\sigma,v} \gamma - V_{s,u} \gamma - V_{\sigma,u} \gamma | \phi_{xy} \rangle \} \\ &- \{ (\gamma_{xy\downarrow}^{EB})^2 [\langle \chi_\pi | h^E - V_{s,u} \gamma^E - V_{\sigma,u} \gamma^E | \chi_\pi \rangle - \langle \phi_{xy} | h^E - V_{s,u} \gamma^E - V_{\sigma,u} \gamma^E | \phi_{xy} \rangle] \\ &- 2\gamma_{xy\downarrow}^{EB} [\langle \chi_\pi | h^E - V_{s,u} \gamma^E - V_{\sigma,u} \gamma^E | \phi_{xy} \rangle - S_\pi \langle \chi_\pi | h^E - V_{s,u} \gamma^E - V_{\sigma,u} \gamma^E | \chi_\pi \rangle] \} \\ &+ \sum_{\substack{i=s, j=\sigma \\ i=\sigma, j=s}} \{ (\gamma_{i,v\downarrow}^B) [\langle \chi_{i,v} | h - V_{s,u} \gamma - V_{\sigma,u} \gamma - \frac{1}{2} V_{j,v} \gamma | \chi_{i,v} \rangle - \langle \phi_v | h - V_{s,u} \gamma - V_{\sigma,u} \gamma - \frac{1}{2} V_{j,v} \gamma | \phi_v \rangle] \\ &- 2\gamma_{i,v\downarrow}^B [\langle \chi_{i,v} | h - V_{s,u} \gamma - V_{\sigma,u} \gamma - \frac{1}{2} V_{j,v} \gamma | \phi_v \rangle - S_i \langle \chi_{i,v} | h - V_{s,u} \gamma - V_{\sigma,u} \gamma - \frac{1}{2} V_{j,v} \gamma | \chi_{i,v} \rangle] \} \\ &+ \sum_{\substack{i=s, j=\sigma \\ i=\sigma, j=s}} \{ (\gamma_{i,u\downarrow}^B)^2 [\langle \chi_{i,u} | h - \frac{1}{2} V_{j,u} \gamma | \chi_{i,u} \rangle - \langle \phi_u | h - \frac{1}{2} V_{j,u} \gamma | \phi_u \rangle] - 2\gamma_{i,u\downarrow}^B [\langle \chi_{i,u} | h - \frac{1}{2} V_{j,u} \gamma | \chi_{i,u} \rangle \\ &- S_i \langle \chi_{i,u} | h - \frac{1}{2} V_{j,u} \gamma | \phi_u \rangle] \} - \sum_{\substack{i=s, j=\sigma \\ i=\sigma, j=s}} \{ (\gamma_{i,u\downarrow}^{EB}) [\langle \chi_{i,u} | h^E - \frac{1}{2} V_{j,u} \gamma^E | \chi_{i,u} \rangle - \langle \phi_u | h^E - \frac{1}{2} V_{j,u} \gamma^E | \phi_u \rangle] \\ &- 2\gamma_{i,u\downarrow}^{EB} [\langle \chi_{i,u} | h^E - \frac{1}{2} V_{j,u} \gamma^E | \chi_{i,u} \rangle - S_i \langle \chi_{i,u} | h^E - \frac{1}{2} V_{j,u} \gamma^E | \phi_u \rangle] \}, \quad (35) \end{aligned}$$

where each sum has but two terms ( $i=s$  and  $j=\sigma$  and vice versa) and where

$$V_i^S = S_i^2 \left[ \int \varphi_i^*(r_2) \frac{1-P_{12}}{r_{12}} \varphi_i(r_2) d\tau_2 + \int \chi_i^*(r_2) \frac{1-P_{12}}{r_{12}} \chi_i(r_2) d\tau_2 \right] - 2S_i \int \varphi_i^*(r_2) \frac{1-P_{12}}{r_{12}} \chi_i(r_2) d\tau_2, \quad (36)$$

$$V_i^\gamma = +2\gamma_i \left[ \int \varphi_i^*(r_2) \frac{1-P_{12}}{r_{12}} \chi_i(r_2) d\tau_2 - S_i \int \chi_i(r_2) \frac{1-P_{12}}{r_{12}} \chi_i(r_2) d\tau_2 \right] + \gamma^2 \left[ \int \varphi_i^*(r_2) \frac{1-P_{12}}{r_{12}} \varphi_i(r_2) d\tau_2 - \int \chi_i^*(r_2) \frac{1-P_{12}}{r_{12}} \chi_i(r_2) d\tau_2 \right], \quad (37)$$

and  $h^E$  is the one-electron Hamiltonian defined for the excited state. The  $\langle |V| \rangle$  integrals in Eq. (35) are the sole remaining interelectronic contributions from Eqs. (33) and (34), all others have cancelled. The first line of Eq. (35) consists of the diagonal crystal field terms; the next two lines are antibonding orbital overlap contributions; lines 4 and 5 are covalent contributions from the unpaired bonding  $t$  and  $e_g$  orbitals involved in the transition<sup>23</sup>; and the last two summations are covalent terms associated with the odd unpaired  $e_u$  bonding electrons. Within the cluster approximation Eq. (35) is an exact expression, to second order, for 10  $Dq$  subject to the following three conditions:

(1) The Hamiltonian must be self-consistently defined for the set of  $\Psi$ 's actually used, in which case Eq. (35) is correct independent of whether the  $\Psi$ 's are, or are not, eigenfunctions of Eq. (6).

(2) The radial behavior of the  $\varphi$  and  $\psi$  atomic orbitals (not necessarily equal to that of free ion H-F functions), must be the same for the two crystal field states, otherwise there are additional contributions to 10  $Dq$ .

(3) It is assumed that the ligand  $1s$  shells do not enter into the bonding. Otherwise, there are additional covalent contributions from unpaired bonding  $\Psi_{1s}^B$  orbitals. Such contributions are straightforwardly added to Eq. (35).

As already noted, the last four lines of Eq. (35) arise from the odd unpaired  $\Psi_{i,u}$  bonding orbitals common to both crystal field states. These and the  $V_{i,u}^\gamma$  contributions to the other lines sum to zero if an excited state parameter  $\gamma_{i,u}^{EB}$  (and its associated matrix elements), equals its ground state,  $\gamma_{i,u}^B$ , counterparts. Assuming this equality to hold, Eq. (35) becomes more simply,

$$10 Dq = \{ \langle \varphi_e | h^E | \varphi_e \rangle - \langle \varphi_t | h | \varphi_t \rangle \} + \{ S_s^2 [ \langle \chi_s | h^E | \chi_s \rangle + \langle \varphi_e | h^E | \varphi_e \rangle ] - 2S_s \langle \chi_s | h^E | \varphi_e \rangle \} \\ + \{ S_\sigma^2 [ \langle \chi_\sigma | h^E | \chi_\sigma \rangle + \langle \varphi_e | h^E | \varphi_e \rangle ] - 2S_\sigma \langle \chi_\sigma | h^E | \varphi_e \rangle \} - \{ S_\pi^2 [ \langle \chi_\pi | h | \chi_\pi \rangle + \langle \varphi_t | h | \varphi_t \rangle ] - 2S_\pi \langle \chi_\pi | h | \varphi_t \rangle \} \\ - \{ (\gamma_{\pi\downarrow}^{EB})^2 [ \langle \chi_\pi | h^E | \chi_\pi \rangle - \langle \varphi_t | h^E | \varphi_t \rangle ] - 2\gamma_{\pi\downarrow}^{EB} \langle \chi_\pi | h^E | \varphi_t \rangle + 2\gamma_{\pi\downarrow}^{EB} S_\pi \langle \chi_\pi | h^E | \chi_\pi \rangle \} \\ + \{ (\gamma_{s\downarrow}^B)^2 [ \langle \chi_s | h | \chi_s \rangle - \langle \varphi_e | h | \varphi_e \rangle ] - 2\gamma_{s\downarrow}^B \langle \chi_s | h | \varphi_e \rangle + 2\gamma_{s\downarrow}^B S_s \langle \chi_s | h | \chi_s \rangle \} \\ + \{ (\gamma_{\sigma\downarrow}^B)^2 [ \langle \chi_\sigma | h | \chi_\sigma \rangle - \langle \varphi_e | h | \varphi_e \rangle ] - 2\gamma_{\sigma\downarrow}^B \langle \chi_\sigma | h | \varphi_e \rangle + 2\gamma_{\sigma\downarrow}^B S_\sigma \langle \chi_\sigma | h | \chi_\sigma \rangle \} \\ + \langle |V_{xy}^\gamma{}^E| \rangle + \langle |V_{e\gamma}| \rangle + \langle |V_{i,v}^S| \rangle. \quad (38)$$

The three  $\langle |V| \rangle$  terms have not been written out explicitly, in anticipation of the fact that we will evaluate this equation in terms of the approximate Hamiltonian,  $h_0$ , which does not contain  $V_s$  and  $V_\gamma$  terms. Hence, the  $\langle |V| \rangle$  corrections of Eqs. (35) and (38) need not be made since these interelectronic effects were not counted twice in our sum over  $\epsilon$ 's. We will thus omit the last line when evaluating Eq. (38) with  $h_0$ . Without these terms, Eq. (38) would be identical with the traditional one given in terms of antibonding covalency, provided that (1) the ground-state unpaired

$\gamma_{s\downarrow}^B$  and  $\gamma_{\sigma\downarrow}^B$  values and their associated matrix elements are identical with those of the excited state  $e_{s\downarrow}^{EA}$  and  $e_{\sigma\downarrow}^{EA}$  electrons and (2) a similar equality holds for the unpaired  $p_{\pi\downarrow}^{EB}$  and  $p_{\pi\downarrow}^A$  contributions. The present calculations indicate that these requirements are not met.

Before closing this section, we should note that, subject to two requirements, the unpaired bonding  $e$  electron covalent mixing contributing to 10  $Dq$  is exactly that which is appropriate to the transferred hyperfine interactions. This differs with the antibonding orbital picture where ground-state antibonding spin  $\uparrow$  covalency contributes to the hyperfine interaction and excited state antibonding spin  $\downarrow$  covalency contributes to 10  $Dq$ . The two requirements are: (1) that the covalent mixing of the two ground-state unpaired  $e^B$  orbitals be identical, a requirement fulfilled by symmetry considerations alone; and (2) that the "odd"  $e^B$  orbitals maintain constant covalency in the two cluster states, for

<sup>23</sup> When treating the covalent mixing of three orbitals (e.g., the  $e_{\downarrow}^A$ ,  $e_{s\downarrow}^B$ ,  $e_{\sigma\downarrow}^B$ ) only two of which (the  $e_{s\downarrow}^B$  and  $e_{\sigma\downarrow}^B$ ) are occupied, there are covalent contributions to a quantity such as 10  $Dq$ . These include, first, the  $\gamma_s$  and  $\gamma_\sigma$  terms of Eq. (35) and second, nonzero  $\gamma_{\sigma s}$  terms [see Eqs. (3)-(5) and related text] caused by nonzero  $s$ - $\sigma$  mixing. The  $\gamma_{\sigma s}$  contributions enter in the third and higher orders in  $\gamma$  and  $S$  and were therefore not listed in Eq. (35). In addition, there are contributions arising from any nonzero overlap of closed  $Ni^{2+}$  shells with ligands, but these appear in third (and higher) order in 10  $Dq$ .

otherwise we have Eq. (35). It is reasonable to assume that this last requirement holds in a lower order theory but that, at some point, we must revert to using Eq. (35) where these orbitals contribute to  $10 Dq$ .

#### VI. THE EVALUATION OF THE COVALENT MIXING AND THE ROLE OF SELF-ENERGY TERMS

We are interested in obtaining the unpaired bonding orbital covalency which contributes to  $10 Dq$  and to transferred hyperfine effects. Also, as noted in Sec. II, independent estimates of the mixing occurring for the members of an antibonding-bonding pair supply us with a test of the internal consistency of our theory. With this factor in mind, we will estimate the covalency of all the occupied bonding and antibonding orbitals in the ground cluster state and of selected ones in the excited state. Let us now consider the process of estimating  $\gamma$ .

As already discussed, we wish to solve the H-F equations [Eq. (6)] defined<sup>24</sup> for the cluster, in a two-function space consisting of  $\varphi_l$  and  $\chi_l$  for the  $l$  mixing, and a three-function space, made up of  $\varphi_e$ ,  $\chi_e$  and  $\chi_\sigma$  for the  $e$  mixing, i.e., we solve  $2 \times 2$  and  $3 \times 3$  secular equations, respectively, for our Hamiltonian  $h$ . For the  $3 \times 3$  solution, we need the matrix elements  $\langle \chi_e | h | \chi_e \rangle$  which were not considered by Sugano and Shulman. As these are intimately associated with the cluster approximation and also include important three- (and four-) center integrals and thereby divert us from the purpose of this paper, we shall not obtain these in the present treatment, deferring this matter, along with others which have been brought up, for a future effort involving the proper Hamiltonian,  $h$ , not  $h_0$ . We will instead explore the consequences of following the traditional view of assuming  $\chi_e - \chi_\sigma$  mixing and overlap to be zero valued (i.e.,  $\gamma_{e\sigma} = \gamma_{\sigma e} = 0$ ). In this approximation we obtain the following relation for any one of the  $\gamma$  values appropriate to Eq. (3):

$$S_i \langle \chi_i | h | \chi_i \rangle - \langle \varphi_i | h | \chi_i \rangle + \gamma_i [\langle \chi_i | h | \chi_i \rangle - \langle \varphi_i | h | \varphi_i \rangle] + \gamma_i^2 [\langle \chi_i | h | \varphi_i \rangle - S_i \langle \varphi_i | h | \varphi_i \rangle] = 0. \quad (39)$$

There are two roots to this equation: The  $|\gamma| < 1$  root is appropriate to the bonding orbital; the other, with  $|\gamma| > 1$ , is appropriate to its orthogonal antibonding partner. Upon dropping the quadratic term, we obtain the Sugano-Shulman relation for  $\gamma_i$ , namely<sup>25</sup> [S&S III, Eq. (2.13)],

$$\gamma_i = \frac{\langle \varphi_i | h | \chi_i \rangle - S_i \langle \chi_i | h | \chi_i \rangle}{\langle \chi_i | h | \chi_i \rangle - \langle \varphi_i | h | \varphi_i \rangle}. \quad (40)$$

<sup>24</sup> Since the antibonding-bonding pair mixing does not contribute to the cluster's total energy, we cannot properly derive the H-F equation appropriate to that mixing for such a derivation must follow from application of the variation principle to the total energy. One can write a one-electron H-F Hamiltonian [Eq. (7)] by inspection and solve for the pair mixing. This we will do but we must remember that the solution has a mathematical but not a physical meaning.

<sup>25</sup> Note the typographical error in the sign of the  $S(\chi|h|\chi)$  term in Eq. (2.13) of S&S III.

They also give a relation for  $\lambda_\pi$  [S&S III, Eq. (2.12)]

$$\lambda_\pi = \frac{\langle \varphi_l | h | \chi_\pi \rangle - S_\pi \langle \varphi_l | h | \varphi_l \rangle}{\langle \chi_\pi | h | \chi_\pi \rangle - \langle \varphi_\pi | h | \varphi_\pi \rangle}, \quad (41)$$

which we find is closely associated with the inverse of the second root of Eq. (39). We will obtain  $\gamma$  values appropriate to both bonding or antibonding mixing. We expect the smaller root of Eq. (39) and the result obtained from Eq. (40) to differ negligibly since the  $\gamma$ 's are small; this will prove to be the case.

As discussed in Sec. III, in computing the matrix elements appearing in Eqs. (38)–(40), our H-F one-electron Hamiltonian,  $h$ , will be replaced by the approximate Hamiltonian  $h_0$ . Now, when evaluating the matrix element of a one-electron H-F Hamiltonian, one often may or may not, as one wishes, include the interelectronic Coulomb and exchange potential terms due to the electron for which the matrix element is being evaluated (in this case  $\Psi_i$ ) because these terms, being equal, cancel one another. The inclusion of such self-energy terms leads to a common Hamiltonian for all electrons in the system, an important and often exploited feature of self-consistent H-F theory.<sup>26,27</sup> If by any chance the cancellation does not occur, these terms *must* be omitted from the Hamiltonian. Such a cancellation does not occur for  $h_0$ , since it is not a self-consistently defined Hamiltonian, and some ambiguity arises concerning the appropriate form of the self-energy term to be subtracted. Consider the evaluation of a matrix element appropriate to an antibonding orbital  $\Psi_i^A$ . The exact self-energy contribution to the potential is

$$\int \Psi_i^{A*}(r_2) \frac{1 - P_{12}}{r_{12}} \Psi_i^A(r_2) d\tau_2, \quad (42)$$

but in view of the fact that  $h_0$  is defined in terms of the (zero overlap) ionic (Ni–F<sub>6</sub>) cluster [i.e., the first line of Eq. (8)], one would be subtracting out terms which did not appear in our Hamiltonian if we subtracted out Eq. (42). A possible choice, *consistent* with using the interelectronic potential of  $h_0$ , is to omit the Coulomb and exchange potential terms associated with the parent  $3d\varphi_i$  (i.e., the overlap ionic counterpart of  $\Psi_i^A$ ), as was done by Sugano and Shulman in the course of estimating antibonding covalency. Likewise, the equivalent  $\chi_i$  contributions would then be omitted when estimating bonding covalency. The use of an approximate Hamiltonian has led to this choice of an approximate self-energy term. We will consider the effect of going to the more exact term after

<sup>26</sup> For example, see A. J. Freeman and R. E. Watson, *Treatise on Magnetism*, edited by G. Rado and H. Suhl (Academic Press Inc., New York, to be published).

<sup>27</sup> Providing that we do not constrain spin pairs of bonding or antibonding orbitals to have the same covalent mixing. Such a requirement would involve us with the nonorthogonality associated with the conventional Hartree-Fock theory (Ref. 26).

first considering the implications of this (zero-overlap) ionic approximation.

The question arises, as to whether the  $p_\pi$  bonding and antibonding matrix elements, for example, evaluated with different self-energy terms will, on insertion into Eqs. (40) and (41), yield  $\lambda_{\pi^A}$  and  $\gamma_{\pi^B}$  values which satisfy the orthogonality relation [cf. Eq. (5)]. A failure to satisfy Eq. (5) may arise from approximations in our Hamiltonian, in the treatment of the self-energy terms or in evaluating matrix elements; but, whatever its source, this failure implies a breakdown of theory. The matrix elements, for bonding and antibonding orbitals, are best compared by writing them for the proper ionic Hamiltonian,  $h_0$  [the first line of Eq. (8) minus the appropriate  $\varphi$  or  $\chi$  self-energy terms] and for a Hamiltonian,  $h_0'$ , without the self-energy subtraction [literally the first line of Eq. (8)]. (Up to this point, we have not considered the role of self-energy terms in discussing the  $h_0$  Hamiltonian. We here redefine  $h_0$  to include the above self-energy term so as to conform to existing usage.) Upon doing this, we have the relations

$$\begin{aligned} \langle \varphi_i | h_0' | \chi_i \rangle^A - \langle \varphi_i | h_0 | \chi_i \rangle^A &= \langle \varphi_i \varphi_i | \varphi_i \chi_i \rangle - \langle \varphi_i \varphi_i | \varphi_i \chi_i \rangle, \\ \langle \varphi_i | h_0' | \chi_i \rangle^B - \langle \varphi_i | h_0 | \chi_i \rangle^B &= \langle \chi_i \chi_i | \chi_i \varphi_i \rangle - \langle \chi_i \chi_i | \chi_i \varphi_i \rangle, \\ \langle \varphi_i | h_0' | \varphi_i \rangle^A - \langle \varphi_i | h_0 | \varphi_i \rangle^A &= \langle \varphi_i \varphi_i | \varphi_i \varphi_i \rangle - \langle \varphi_i \varphi_i | \varphi_i \varphi_i \rangle, \\ \langle \chi_i | h_0' | \chi_i \rangle^B - \langle \chi_i | h_0 | \chi_i \rangle^B &= \langle \chi_i \chi_i | \chi_i \chi_i \rangle - \langle \chi_i \chi_i | \chi_i \chi_i \rangle. \end{aligned} \quad (43)$$

The integrals on the right-hand side of Eq. (43), coming from the Coulomb and exchange self-energy terms, obviously cancel, indicating that these matrix elements are independent of whether such terms are included in the Hamiltonian. However, we also have

$$\begin{aligned} \langle \varphi_i | h_0' | \varphi_i \rangle^B - \langle \varphi_i | h_0 | \varphi_i \rangle^B &= \langle \varphi_i \varphi_i | \chi_i \chi_i \rangle - \langle \varphi_i \chi_i | \varphi_i \chi_i \rangle, \\ \langle \chi_i | h_0' | \chi_i \rangle^A - \langle \chi_i | h_0 | \chi_i \rangle^A &= \langle \varphi_i \varphi_i | \chi_i \chi_i \rangle - \langle \varphi_i \chi_i | \varphi_i \chi_i \rangle, \end{aligned} \quad (44)$$

and here the cancellation of terms does not occur. Noting that the bonding and antibonding matrix elements of  $h_0'$  are, by definition, identical, gives us the following relationships between bonding and antibonding  $h_0$  behavior for a bonding-antibonding pair:

$$\begin{aligned} \langle \varphi_i | h_0 | \chi_i \rangle^A &= \langle \varphi_i | h_0 | \chi_i \rangle^B, \\ \langle \varphi_i | h_0 | \varphi_i \rangle^A &= \langle \varphi_i | h_0 | \varphi_i \rangle^B + \langle \varphi_i \varphi_i | \chi_i \chi_i \rangle - \langle \varphi_i \chi_i | \varphi_i \chi_i \rangle, \\ \langle \chi_i | h_0 | \chi_i \rangle^A &= \langle \chi_i | h_0 | \chi_i \rangle^B - \langle \varphi_i \varphi_i | \chi_i \chi_i \rangle + \langle \varphi_i \chi_i | \varphi_i \chi_i \rangle. \end{aligned} \quad (45)$$

The two-electron integrals are most definitely nonzero.<sup>28</sup>

<sup>28</sup> The fact that self-energy terms cause  $\langle |h\rangle^B$  matrix elements to differ from their  $\langle |h\rangle^A$  counterparts is, in itself, a necessary but not sufficient condition for a computed  $\gamma^A$  to differ from  $\gamma^B$ . A computation with the exact one-electron Hamiltonian and with the exact self-energy terms [Eq. (42)] will have  $\langle |h\rangle^B \neq \langle |h\rangle^A$  for the  $\langle \chi | h | \chi \rangle$ ,  $\langle \chi | h | \varphi \rangle$  and  $\langle \varphi | h | \varphi \rangle$  matrix elements, one will obtain identical  $\gamma$  values. In the present case, the differences, in  $\langle \varphi | h_0 | \chi \rangle$  matrix elements will be seen to cause severe differences between a  $\gamma^A$  and its partner  $\gamma^B$ .

But, what is more important, we will see that the  $\langle |h_0\rangle^A$ 's, on insertion into, say, Eq. (39) yield a different  $\gamma$  than do the  $\langle |h_0\rangle^B$ 's. This means that the theory, with its present approximations, fails to yield the required bonding-antibonding pair orthogonality. We will see this failure to be severe.

Not only does the theory suffer this internal inconsistency but it is difficult to ascertain which of the approximations is most at fault. Use of the full Hamiltonian of Eq. (8), the exact self-energy term [Eq. (42)], and extreme care in the evaluation of matrix elements would resolve this problem but would also be beyond the scope of this paper. We do wish to inspect one feature of the theory here, namely, given a Hamiltonian (in this case  $h_0'$ ), what part do the self-energy terms play in the behavior of individual matrix elements and, in turn, on the resulting estimates of covalency. Such an investigation will further indicate the nature of the computed covalency and its sensitivity to computational details (including assumed covalency) while enabling us to avoid the serious numerical problems associated with a proper treatment with the proper covalent Hamiltonian. We believe this to justify a partial handling of the problem.

Let us define a Hamiltonian,  $H$ , which is equal to  $h_0'$  minus self-energy terms defined for the covalent  $\Psi_i$ 's in Eq. (42). One may then obtain equations similar to (43) or (44) such as

$$\begin{aligned} \langle \varphi_i | h_0' | \chi_i \rangle^A - \langle \varphi_i | H | \chi_i \rangle^A &= N_i \{ \langle \varphi_i \varphi_i | \varphi_i \chi_i \rangle - \langle \varphi_i \varphi_i | \varphi_i \chi_i \rangle - 2\lambda_i \langle \varphi \chi | \varphi \chi \rangle \\ &\quad + \lambda_i \langle \varphi \chi | \varphi \chi \rangle + \lambda_i \langle \varphi \varphi | \chi \chi \rangle + \lambda_i^2 \langle \chi \chi | \varphi \chi \rangle \\ &\quad - \lambda_i^2 \langle \chi \varphi | \chi \chi \rangle \} \\ &= -\lambda_i \{ \langle \varphi \chi | \varphi \chi \rangle - \langle \varphi \varphi | \chi \chi \rangle \} + O(\lambda^3) \end{aligned} \quad (46)$$

or

$$\langle \varphi_i | H | \chi_i \rangle^A = \langle \varphi_i | h_0 | \chi_i \rangle^A - \lambda_i \{ \langle \varphi_i \varphi_i | \chi_i \chi_i \rangle - \langle \varphi_i \chi_i | \varphi_i \chi_i \rangle \}. \quad (47)$$

For the other matrix elements we obtain

$$\begin{aligned} \langle \varphi_i | H | \chi_i \rangle^B &= \langle \varphi_i | h_0 | \chi_i \rangle^B + \gamma_i \{ \langle \varphi_i \varphi_i | \chi_i \chi_i \rangle \\ &\quad - \langle \varphi_i \chi_i | \varphi_i \chi_i \rangle \}, \\ \langle \varphi_i | H | \varphi_i \rangle^A &= \langle \varphi_i | h_0 | \varphi_i \rangle^A - \lambda_i^2 \{ \langle \varphi_i \varphi_i | \chi_i \chi_i \rangle \\ &\quad - \langle \varphi_i \chi_i | \varphi_i \chi_i \rangle \}, \\ \langle \chi_i | H | \chi_i \rangle^A &= \langle \chi_i | h_0 | \chi_i \rangle^A + [1 - N_i^2] \\ &\quad \times \{ \langle \varphi_i \varphi_i | \chi_i \chi_i \rangle - \langle \varphi_i \chi_i | \varphi_i \chi_i \rangle \}, \quad (48) \\ \langle \varphi_i | H | \varphi_i \rangle^B &= \langle \varphi_i | h_0 | \varphi_i \rangle^B + [1 - (N_i')^2] \\ &\quad \times \{ \langle \varphi_i \varphi_i | \chi_i \chi_i \rangle - \langle \varphi_i \chi_i | \varphi_i \chi_i \rangle \}, \\ \langle \chi_i | H | \chi_i \rangle^B &= \langle \chi_i | h_0 | \chi_i \rangle^B - \gamma_i^2 \{ \langle \varphi_i \varphi_i | \chi_i \chi_i \rangle \\ &\quad - \langle \varphi_i \chi_i | \varphi_i \chi_i \rangle \}, \end{aligned}$$

where terms of order  $\lambda^3$ ,  $\gamma^3$ , or higher have been dropped. We will report solutions of Eq. (39) utilizing the linear covalent contributions to the off-diagonal  $\langle \varphi | H | \chi \rangle^A$  and  $\langle \varphi | H | \chi \rangle^B$  matrix elements (omitting second and

higher order corrections). We will see the computed covalency to be sensitive to the estimates of covalency used in evaluating these matrix elements.

We have so far considered the differences which do, but should not, occur in the estimates appropriate to members of a bonding-antibonding pair. Let us now consider how these do (and should) differ with that appropriate to an unpaired bonding orbital. When obtaining the  $\langle \varphi_i | h | \varphi_i \rangle$  and  $\langle \varphi_i | h | \chi_i \rangle$  matrix elements for either member of a bonding-antibonding pair, the Coulomb and exchange contributions of  $\varphi_i$  to  $V_m$  [see Eq. (9)] cancel after the manner of the right-hand sides of Eqs. (43). The Coulomb repulsions of the seven other Ni 3*d* electrons remain, and the potential contributed by the Ni ion to these matrix elements is that characteristic of Ni<sup>2+</sup>. However, no such cancellation occurs when evaluating the same matrix elements for an unpaired bonding orbital because the  $\varphi_i$  involved in the bonding is not one of the eight contributing to the Ni potential. Eight 3*d* electrons make Coulomb contributions in this case, causing the potential to be characteristic of Ni<sup>+</sup>, not of Ni<sup>2+</sup>. [Such a 3*d* electron Coulomb contribution to  $\langle \varphi | h | \varphi \rangle$  which is  $\sim 1$  a.u., is to be compared with (1) the denominators of Eq. (40) which are as small as 0.25 a.u., (2) the  $\langle \varphi \varphi | \chi \chi \rangle$  Coulomb self-energy terms of Eqs. (44) and (45), which are  $\sim 0.3$  a.u. and (3) 3*d*-3*d* exchange interactions, which are the order of 0.1 a.u.] It must be emphasized that this difference occurs whether we evaluate matrix elements with  $h_0$  or with the exact self-consistent Hamiltonian  $h$ . In other words, such an effect on the current results involving  $h_0$ , is indicative of what actually occurs for the exact self-consistent LCAO treatment of the cluster.

From our experience with the potential terms of Sec. III, we should have anticipated the differences in the Ni potentials appropriate to the various  $\langle \varphi | h | \varphi \rangle$  and  $\langle \varphi | h | \chi \rangle$  matrix elements. The fact that these differences occur is a key to the intrinsically different nature of the covalency of a bonding-antibonding pair on one hand and an unpaired bonding orbital on the other. The magnitude (1 a.u.) of the difference in the  $\langle \varphi | h | \varphi \rangle$  matrix elements has observable quantitative repercussions on one's theoretical estimates and makes it imperative that the pertinent covalent mixing be investigated.

## VII. THE MATRIX ELEMENTS

In this section we evaluate the  $h_0$  matrix elements appropriate to the various bonding and antibonding cases of interest, and examine the effects due to the net 3*d* spin on the Ni<sup>2+</sup> ion. Wherever possible, we will rely on the one- and two-electron integrals already obtained in S&S III and the same approximations have been made when evaluating the  $V_L$  matrix elements. The additional required integrals have been evaluated with conventional (or restricted) analytic H-F (hence-

TABLE I. The one-electron energies (Ref. 32) of the RHF 3*d* orbitals, for the  ${}^3F(M_L=L, M_S=S)$  state of Ni<sup>2+</sup>, as defined by Eq. (52). In these tables, the appropriate  $m_s$  value is denoted by the arrow ( $\uparrow$  and  $\downarrow$  denote  $m_s = \frac{1}{2}$  and  $-\frac{1}{2}$ , respectively). Also included is the  $\epsilon_{\text{RHF}}$  value. All quantities are in atomic units.

$\epsilon_{3d}$	$m_s =$	$\uparrow$	$\downarrow$
$m_l = 2$		-1.46199	-1.39472
1		-1.44377	-1.34007
0		-1.41399	-1.34007
-1		-1.44377	-0.38057
-2		-1.46199	-0.38057
$\epsilon_{\text{RHF}} = -1.41254$			

forth denoted as RHF) functions for<sup>29</sup> Ni<sup>2+</sup> and<sup>30</sup> F<sup>-</sup>. However, no additional three- and four-center integrals were obtained for this work although they are required in a proper treatment of the theory. The Switendick-Corbato IBM 7090 program<sup>31</sup> was used for such two-center integrals as arose.

### A. $\langle \varphi_i | h_0 | \varphi_i \rangle$

It is in this matrix element that 3*d* shell exchange and Ni<sup>+</sup> versus Ni<sup>2+</sup> potential repercussions are most important. We are constructing our molecular orbitals from free ion H-F orbitals and this suggests that we make use of the familiar<sup>25</sup> one-electron Hartree-Fock equation,

$$\mathcal{H}_{\text{Ni}} \varphi_i(\mathbf{r}, \boldsymbol{\sigma}) = \epsilon_i \varphi_i(\mathbf{r}, \boldsymbol{\sigma}), \quad (49)$$

when evaluating  $\langle \varphi_i | h_0 | \varphi_i \rangle$ . Here  $\varphi_i$  is a one-electron spin orbital (i.e., a function of space and spin),  $\epsilon_i$  is its H-F energy eigenvalue, and  $\mathcal{H}_{\text{Ni}}$  is the one-electron H-F Hamiltonian for Ni<sup>2+</sup>, consisting of kinetic, nuclear potential, and interelectronic Coulomb and exchange terms. With the self-energy terms included,  $\mathcal{H}_{\text{Ni}}$  is independent<sup>26</sup> of which Ni<sup>2+</sup> orbital it operates on and is related to  $h_0'$  by

$$h_0' = \mathcal{H}_{\text{Ni}} + V_L(r). \quad (50)$$

Since our 3*d*  $\varphi_i$ 's are RHF functions this suggests that we simply have

$$\langle \varphi_i | h_0' | \varphi_i \rangle = \epsilon_{\text{RHF}} + \langle \varphi_i | V_L | \varphi_i \rangle, \quad (51)$$

where  $\epsilon_{\text{RHF}}$  is the 3*d* eigenvalue. Unfortunately, this equation does not hold, for the RHF Ni<sup>2+</sup>  $\varphi$ 's are not exact eigenfunctions of Eq. (49). RHF theory requires<sup>26</sup> a single radial function per shell. For an open-shell ion this is only obtained by constraints, for there exists no single radial function which, when inserted into the occupied  $\varphi_i$ 's, will satisfy Eq. (49) for all electrons in a shell. The immediate implications of this can be seen by first inspecting Table I where the values<sup>32</sup> of

$$\epsilon_i \equiv \langle \varphi_i | \mathcal{H}_{\text{Ni}} | \varphi_i \rangle \quad (52)$$

<sup>29</sup> R. E. Watson, Technical Report No. 12, Solid-State and Molecular Theory Group, MIT, 1959 (unpublished).

<sup>30</sup> C. Sonnenschein (unpublished).

<sup>31</sup> A. C. Switendick and F. J. Corbato, Quarterly Progress Report No. 34, Solid-State and Molecular Theory Group, MIT, October 1959 (unpublished).

<sup>32</sup> See p. 229 of Ref. 29.

TABLE II. One-electron energies for the cubic  $3d$  orbitals of  $\text{Ni}^{2+}$  as defined by Eq. (52) for the configurations indicated in the text. All quantities are in atomic units.

$\epsilon_{i\uparrow} = -1.42742$	$\epsilon_{e\downarrow} = -0.38057$
$\epsilon_{i\downarrow} = -1.35829$	$\epsilon_{e\downarrow}^B = -1.35829$
$\epsilon_{e\uparrow} = -1.47226$	$\epsilon_{i\downarrow}^B = -0.38057$
$\epsilon_{\text{RHF}} = -1.41254$	

for the various occupied and unoccupied  $3d$  orbitals of the RHF  $\text{Ni}^{2+}$  ion are listed. Also included is  $\epsilon_{\text{RHF}}$ , which was used in S&S III when evaluating Eq. (51) for  $\langle \varphi_i | h_0 | \varphi_i \rangle$ . We see that the occupied orbital  $\epsilon_i$ 's vary by as much as 0.12 a.u. Energy denominators as small as 0.22 a.u. occur in Eqs. (40) and (41), suggesting that these variations can observably affect the evaluation of these equations. One notes that the smaller  $\epsilon_i$ 's occur for occupied  $3d$  orbitals of minority spin as one would expect since exchange lowers an electron's energy. The unoccupied orbital  $\epsilon$ 's lie approximately 1 a.u. higher than the others and show (cf. the discussion in the preceding section) the Coulomb energy penalty of attempting to place a ninth  $3d$  electron on the ion. This penalty, which the unpaired bonding orbital covalency must pay, greatly influences results.

One may rigorously use Eq. (51) providing one inserts the  $\epsilon_i$ , defined by Eq. (52) for the orbital and multi-electron Ni state of interest. The  $\epsilon_i$ 's of interest are readily obtained with the available<sup>29</sup> integrals and are listed in Table II. The resulting  $\langle \varphi_i | h_0 | \varphi_i \rangle$ 's evaluated using Eq. (51), with self-energy terms properly accounted for and utilizing the S&S III approximate values for the  $\langle \varphi_i | V_L | \varphi_i \rangle$ 's are given in Table III. Also listed for comparison are the matrix elements as obtained by Sugano and Shulman; these are  $\langle \varphi_i | h_0 | \varphi_i \rangle^A$  values.

### B. $\langle \chi_i | h_0 | \varphi_i \rangle$

If one assumes Eq. (49) to hold, then these matrix elements are obtained by first evaluating

$$\begin{aligned} \langle \chi_i | h_0' | \varphi_i \rangle &= \langle \chi_i | \mathcal{H}_{\text{Ni}} | \varphi_i \rangle + \langle \chi_i | V_L | \varphi_i \rangle \\ &= \epsilon_{\text{RHF}} S_i + \langle \chi_i | V_L | \varphi_i \rangle. \end{aligned} \quad (53)$$

 TABLE III. The matrix elements  $\langle \varphi | h_0 | \varphi \rangle$  for bonding ( $B$ ), antibonding ( $A$ ), and excited configuration ( $E$ ) covalent mixing. All quantities are in atomic units.

		S&S III values			
$i\uparrow^A$	0.1216	(0.1365)	$i\uparrow^B$	-0.1358	
$i\downarrow^A$	0.1907	(0.1365)	$i\downarrow^B$	-0.0667	
$e\uparrow^A$	( $s$ or $p\sigma$ )	(0.1202)	$e\uparrow^B(s)$	-0.2058	
			$e\uparrow^B(p\sigma)$	-0.2178	
$e\downarrow^{EA}$	0.1744	(0.1202)	$e\downarrow^{EB}(s)$	-0.0918	
			$e\downarrow^{EB}(p\sigma)$	-0.1038	
			$e\downarrow^B(s)$	0.8859	
			$e\downarrow^B(p\sigma)$	0.8739	
			$i\downarrow^{EB}$	0.9110	

But since the  $\varphi_i$ 's are not exact eigenfunctions of that equation, the  $\langle \chi_i | \mathcal{H}_{\text{Ni}} | \varphi_i \rangle$  contribution should not be estimated in this way. This contribution has, with one approximation, been evaluated explicitly and the results appear in Table IV. The one approximation, necessitated by numerical inaccuracies in the  $1s$  integral, consists of omitting the Coulomb potential term due to

 TABLE IV. Values of  $\langle \chi_i | \mathcal{H}_{\text{Ni}} | \varphi_i \rangle$  and  $\epsilon_{\text{RHF}} S_i$  (with  $S_i$  taken from S&S III) for ground and excited ( $E$ ) configuration covalent mixing. All quantities are in atomic units.

	$\langle \chi_i   \mathcal{H}_{\text{Ni}}   \varphi_i \rangle$	$\epsilon_{\text{RHF}} S_i$
$i\uparrow$	-0.10528	-0.1067
$i\downarrow$	-0.10406	-0.1067
$e\uparrow(s)$	-0.11751	-0.1150
$e\uparrow(p\sigma)$	-0.15150	-0.1564
$e\downarrow^B(s)$	-0.11751	-0.1150
$e\downarrow^B(p\sigma)$	-0.14695	-0.1564
$e\downarrow(s)$	-0.08478	...
$e\downarrow(p\sigma)$	-0.09572	...
$i\downarrow^B$	-0.0739	

the  $1s^2$  shell, and compensating for this with a nuclear potential term for a nuclear charge two less than that of Ni. Otherwise, the Switendick-Corbato program was used to obtain all integrals occurring in the  $\langle \chi_i | \mathcal{H}_{\text{Ni}} | \varphi_i \rangle$ 's. The  $\epsilon_{\text{RHF}} S_i$  products are included in Table IV and we see that these differ but slightly from the exact values, indicating that assuming Eq. (42) has less significant repercussions here than it does for  $\langle \varphi | h | \varphi \rangle$  matrix elements.

Using the S&S III estimates of the  $\langle \chi_i | V_L | \varphi_i \rangle$  contributions, the  $\langle \chi_i | h_0 | \varphi_i \rangle$  matrix elements are given in Table V. As we see from Eqs. (45), these matrix

 TABLE V. The matrix elements  $\langle \chi_i | h_0 | \varphi_i \rangle$  for ground and excited ( $E$ ) configuration covalent mixing.<sup>a</sup> All quantities are in atomic units.

	Present calculation	S&S III
$i\uparrow$	-0.0428	(-0.0443)
$i\downarrow$	-0.0416	
$e\uparrow(s)$	-0.1185	(-0.1160)
$e\uparrow(p\sigma)$	-0.0937	(-0.0986)
$e\downarrow^B(s)$	-0.1185	
$e\downarrow^B(p\sigma)$	-0.0891	
$e\downarrow(s)$	-0.0858	
$e\downarrow(p\sigma)$	-0.0379	
$i\downarrow^B$	-0.0115	

<sup>a</sup> These matrix elements are independent of whether we are dealing with bonding or antibonding effects (see text).

elements, unlike  $\langle \chi | h_0 | \chi \rangle$  and  $\langle \varphi | h_0 | \varphi \rangle$ , are independent of whether we are dealing with bonding or antibonding orbitals. The matrix elements are sensitive to whether they are for an antibonding-bonding pair or for an unpaired bonding orbital [ $e(s)\uparrow$ ,  $e(p\sigma)\downarrow$ , and  $i\downarrow^B$ ]. We see values for the latter to be appreciably smaller in magnitude.

C.  $\langle \kappa_i | h_0 | \kappa_i \rangle$ 

The various values of this matrix element are readily obtained using the integrals appearing<sup>33</sup> in Table II of S&S III. The results appear in Table VI. Two features of the matrix element behavior should be noted. First, as expected, unlike the cases of  $\langle \chi | h_0 | \varphi \rangle$  and  $\langle \varphi | h_0 | \varphi \rangle$  matrix elements, the  $\langle \chi | h_0 | \chi \rangle$  matrix elements appropriate to the unpaired bonding orbitals differ but trivially from the paired bonding orbital values. This small difference indicates that these matrix elements cannot compensate for the shifts, appearing in the unpaired bonding  $\langle \varphi | h_0 | \chi \rangle$  and  $\langle \varphi | h_0 | \varphi \rangle$  values, due to

TABLE VI. The matrix elements  $\langle \chi_i | h_0 | \chi_i \rangle$  for bonding (*B*), antibonding (*A*) and excited configuration (*E*) covalent mixing. All quantities are in atomic units.

$t_{\uparrow}^A$	-0.0837		$t_{\uparrow}^B$	+0.1737
$t_{\downarrow}^A$	-0.0835	(-0.0835)	$t_{\downarrow}^B$	+0.1739
$e_{\uparrow}^A(s)$	-0.9965		$e_{\uparrow}^B(s)$	-0.7303
$e_{\uparrow}^A(p_{\sigma})$	-0.1659		$e_{\uparrow}^B(p_{\sigma})$	+0.1123
$e_{\uparrow}^{EA}(s)$	-0.9959	(-0.9959)	$e_{\downarrow}^{EB}(s)$	-0.7297
$e_{\uparrow}^{EA}(p_{\sigma})$	-0.1628	(-0.1628)	$e_{\downarrow}^{EB}(p_{\sigma})$	+0.1154
			$e_{\downarrow}^B(s)$	-0.7300
			$e_{\downarrow}^B(p_{\sigma})$	+0.1162
			$t_{\downarrow}^{EB}$	+0.1753

the Ni<sup>+</sup> potential. Secondly, we see a sign reversal, similar to the one in Table II, on going from the antibonding to the bonding member of a  $p_{\pi}$  or  $p_{\sigma}$  pair, which is again due to the self-energy terms of Eqs. (45). Their effect is to reverse the sign of the denominator of Eq. (40) and of the linear term of Eq. (39), a feature which will be of great importance to us when discussing results.

D. The Overlap Integrals,  $S_i$ 

As already noted, the present investigation has utilized analytic HF functions in its evaluation of integrals. Sugano and Shulman used the same Ni 3*d*, but different F<sup>-</sup>, orbitals. They used simple two-exponential analytic approximations to the F<sup>-</sup> functions of Froese,<sup>34</sup> a choice which was necessitated by the extensive nature of the computations.  $S_i$  values which

TABLE VII. Comparison of overlap integrals obtained by S&S III and in this calculation.

	This calculation	S&S III
$S_i$	0.07077	0.07557
$S_{\sigma}(s)$	0.07977	0.08143
$S_{\sigma}(p_{\sigma})$	0.10499	0.11071

<sup>33</sup> Two additional integrals are needed. Their values, in the notation of the S&S III Appendix, are:  $(d\sigma, p\pi^+ || d\delta^+, p\pi^-) = -0.000255$  a.u.  $(d\sigma, p\pi^+ || p\pi^-, d\delta^+) = 0.000039$  a.u. The  $\langle \chi | h_0 | \chi \rangle$  integrals are the most seriously affected by the (almost) complete omission (Ref. 10) of three and four-center integrals.

<sup>34</sup> C. Froese, Proc. Cambridge Phil. Soc. 53, 206 (1957).

were obtained for the current set of functions, along with their S&S III counterparts, are listed in Table VII; the differences serve as a measure of the error, due to wave function uncertainty, that should be attached to such integrals as these. The  $S_i$  obtained with Sonenschein's F<sup>-</sup> orbitals will be used in the following section.

E.  $\langle |H| \rangle$ 

From the definitions of Eqs. (47) and (48), we see that these matrix elements are functions of covalency and as we will want them for varying  $\gamma$  and  $\lambda$  values, we list in Table VIII the terms

$$[\langle \varphi_i \varphi_i | \chi_i \chi_i \rangle - \langle \varphi_i \chi_i | \varphi_i \chi_i \rangle],$$

which are necessary for evaluating these equations and the corresponding terms of Eq. (45) (used in the evaluation of Tables III and VI). These were obtained from integrals appearing in S&S III, which only include two-center integral contributions. It should be noted that by basing these terms on two-center integrals alone, we are making ligand  $\chi$  self-energy corrections [the first equation of (44)] which are strictly compatible with the  $V_L$  in our  $h_0$  Hamiltonian. Here too, the inclusion of three-center contributions to these integrals may have appreciable quantitative effects on these terms. In the calculations which follow, we will keep only the linear covalent contributions occurring in the  $\langle \varphi_i | H | \chi_i \rangle$  matrix elements; the other elements will then keep their  $h_0$  values. In view of our decision not to use a proper covalent Hamiltonian in this paper, a more detailed treatment seems unjustified.

## VIII. RESULTS

Equations (39) and (40) have been evaluated with the  $h_0$  matrix elements of the preceding section for the various bonding and antibonding  $\gamma$ 's. The results appear in Table IX. Only the  $\gamma$ 's, which are less than 1 in magnitude, have been reported for Eq. (39); as stated earlier, the larger roots are redundant.

An important feature of the results in Table IX concerns the internal consistency of a theory relying on  $h_0$ . We see that the  $\gamma_i^A$  and  $\gamma_i^B$ , of a  $p_{\sigma}$  or  $p_{\pi}$  antibonding-bonding pair, differ in sign while those for  $s$  bonding differ in magnitude. As we have already stressed, a  $\gamma_i^A$  must equal its partner  $\gamma_i^B$  if the orthogonality requirements of Eqs. (5) are to be realized. Any failure to meet these requirements implies a

TABLE VIII. The  $[\langle \varphi_i \varphi_i | \chi_i \chi_i \rangle - \langle \varphi_i \chi_i | \varphi_i \chi_i \rangle]$  values necessary for obtaining the covalent contributions to the  $\langle |H| \rangle$  matrix elements. All quantities are in atomic units.

$i$	$[\langle \varphi_i \varphi_i   \chi_i \chi_i \rangle - \langle \varphi_i \chi_i   \varphi_i \chi_i \rangle]$
$e(s)$	0.26618
$e(p_{\sigma})$	0.27823
$t(p_{\pi})$	0.25741

TABLE IX. The  $\gamma_i$  covalent mixing parameters, as estimated with Eqs. (39) and (40), for bonding ( $B$ ), antibonding ( $A$ ) and excited configuration ( $E$ ) cases, and compared with the S&S III values.

		Eq. (40)	Eq. (39)	S&S III values		Eq. (40)	Eq. (39)
$t\uparrow^A$		0.180	0.171		$t\uparrow^B$	-0.178	-0.174
$t\downarrow^A$	c	0.130	0.127	(0.1727)	$t\downarrow^B$	-0.224	-0.217
$e\uparrow^A(s)$	d	0.037	0.037		$e\uparrow^B(s)$	0.114	0.112
$e\uparrow^A(p_\sigma)$	d	0.337	0.298		$e\uparrow^B(p_\sigma)$	-0.319	-0.287
$e\downarrow^{EA}(s)$	c	0.033	0.033	(0.0313)	$e\downarrow^{EB}(s)$	0.094	0.093
$e\downarrow^{EA}(p_\sigma)$	c	0.214	0.201	(0.2848)	$e\downarrow^{EB}(p_\sigma)$	-0.462	-0.404
					$e\downarrow^B(s)$	0.0171	0.0169
					$e\downarrow^B(p_\sigma)$	0.0661	0.0654
					$t\downarrow^{EB}$	0.0325	0.0322

<sup>a</sup> Contribute to 10  $Dq$ .

<sup>b</sup> Contribute to transferred hyperfine effects.

<sup>c</sup> Contribute to 10  $Dq$  in the traditional antibonding model.

<sup>d</sup> Contribute to the transferred hyperfine effects in the traditional antibonding model.

breakdown of the theory. The deviations seen in Table IX lead to antibonding-bonding orthogonality integrals as large as 0.6 instead of the required zero. Thus, the severity of this orthogonality breakdown renders any quantity estimated with these  $\gamma$ 's at best suspect.

The  $\gamma_p$  sign reversals of Table IX have been caused by the reversal in sign of the  $[\langle\chi|h_0|\chi\rangle - \langle\varphi|h_0|\varphi\rangle]$  term of Eqs. (39)–(41), due to self-energy effects. We expect a similar sign reversal in this term if we go to a theory utilizing the exact self-consistent Hamiltonian (and the exact self-energy expressions). The only way in which this exact theory can then yield a common  $\gamma_p^A$  and  $\gamma_p^B$  will be if  $\langle\varphi|h|\chi\rangle$  reverses sign as well (note that here we refer to a matrix element of  $h$ , not  $h_0$ ). We will shortly see indications that this does indeed occur.

Three other features of the results of Table IX should be viewed before we leave them. First, Eq. (40) and the more exact (39) give results of similar character but occasionally differ by as much as 10%. Secondly, the difference in  $\gamma$ 's, for pairs of orbitals differing only in spin, are not negligible. These do not affect our predictions for  $\text{Ni}^{2+}$  but such effects are of sufficient magnitude to observably affect the transferred hyperfine spectrum associated with an ion such as  $\text{Cr}^{3+}$  (cf. Sec. IV). Finally, we see the unpaired bonding orbital  $\gamma$  values to be appreciably smaller than their paired orbital antibonding counterparts, suggesting that one must not assume them equivalent and that one must utilize the unpaired bonding results when estimating 10  $Dq$  or some other experimental parameter. The large uncertainty which one must attach to the antibonding  $\gamma$ 's (due to the antibonding-bonding pair breakdown) makes this comparison tenuous. The results which we will now inspect, also indicate substantial differences between the  $\gamma^A$  and unpaired  $\gamma^B$  behavior.

We are not prepared in the present paper to attempt a calculation involving the full Hamiltonian,  $h$ , of Eq. (8), but we do wish to gain some idea of the sensitivity of the predictions to covalency. To do this we will go over to the covalent treatment of the self-energy correction, utilizing the  $H$  matrix elements of Eqs. (47)

and (48) (actually we will only consider the linear contributions to the  $\langle\varphi|H|\chi\rangle$ 's). Computing  $\gamma_i$ 's as a function of assumed  $\gamma^0$  values (appearing in  $\langle\varphi|H|\chi\rangle$ ), we obtain the results of Table X. We see that the bonding-antibonding pair results are quite sensitive to this covalent contribution and that the negative  $\gamma$ 's turn positive with increasing covalency because of a sign reversal in the  $\langle\varphi|H|\chi\rangle$  elements. Since we have not used the proper Hamiltonian, we cannot expect complete convergence of the  $p$  electron bonding-antibonding  $\gamma_i$  pairs. The table also suggests that, given the Hamiltonian, we have underestimated the bonding-antibonding covalency if we use the antibonding results of Table IX.

In contrast with the paired bonding behavior, the unpaired bonding  $\gamma$ 's of Table X show a tendency of  $\langle\varphi|H|\chi\rangle$  to reverse sign. The  $(\langle\chi|h_0|\chi\rangle - \langle\varphi|h_0|\varphi\rangle)$  term does not have a negative sign (as do the paired bonding elements), and this causes the trend toward negative  $\gamma$ 's. The tendency towards increased paired orbital  $\gamma$ 's and decreased unpaired bonding  $\gamma$ 's serves to accentuate the different nature of the two types of covalent mixing.

 TABLE X. The covalent mixing  $\gamma_i$ , as estimated using Eq. (39) with  $\langle\varphi_i|H|\chi_i\rangle$  matrix elements for bonding ( $B$ ), antibonding ( $A$ ), and excited configuration ( $E$ ) cases as a function of assumed covalency.

	Assumed $\gamma_i^0$						
	0	0.05	0.1	0.2	0.3	0.4	0.5
$e\uparrow^A(s)$	0.057	0.069	0.081	...	...	...	...
$e\uparrow^B(s)$	0.112	0.088	0.064	...	...	...	...
$e\uparrow^A(\sigma)$	0.38	...	0.44	0.50	0.55	0.59	0.62
$e\uparrow^B(\sigma)$	-0.30	...	-0.23	-0.15	-0.07	0.017	0.10
$t\uparrow^A$	0.24	...	0.34	0.42	0.48	0.53	0.58
$t\uparrow^B$	-0.17	...	-0.094	-0.12	-0.07	0.15	0.22
$t\downarrow^A$	0.19	...	0.27	0.33	0.39	0.44	0.49
$t\downarrow^B$	-0.22	...	-0.12	-0.10	-0.096	0.19	0.28
$e\downarrow^{EA}(\sigma)$	0.27	...	0.33	0.38	0.43	0.47	0.50
$e\downarrow^{EB}(\sigma)$	-0.40	...	-0.31	-0.20	-0.086	0.046	0.16
$e\downarrow^{EA}(s)$	0.051	0.062	0.073	...	...	...	...
$e\downarrow^{EB}(s)$	0.093	0.073	0.053	...	...	...	...
$e\downarrow^B(s)$	0.017	0.009	0.0008	-0.016	...	...	...
$e\downarrow^B(\sigma)$	0.065	0.047	0.0295	-0.007	...	...	...
$t\downarrow^{EB}$	0.032	0.015	0.0030	-0.033	...	...	...



TABLE XI. The covalent mixing parameters,  $\gamma_i$ , as estimated using Eq. (39) with  $\langle\varphi_i|H|\chi_i\rangle$  matrix elements for the unpaired  $t_4^{B^B}$ ,  $e_4^B(s)$ , and  $e_4^B(\sigma)$  orbitals for assumed  $\gamma_i^0$  values.

	Input $\gamma_i^0$	Computed $\gamma_i$
$e_4^B(s)$	0.01	0.015 <sub>4</sub>
$e_4^B(\sigma)$	0.05	0.047
$t_4^{B^B}$	0.025	0.0236

In Table XI we have reevaluated the unpaired  $\gamma$ 's with input  $\langle\varphi|H|\chi\rangle$  covalent contributions suggested by Table X. The results show internal consistency and are in crude agreement with the noncovalent estimates of Table IX. This is largely due to the fact that the covalency is small and hence the covalent self-energy repercussions are small (but not insignificant).

So far we have only considered the occupied orbitals of the cluster and have not used the alternate approach of dealing with the antibonding holes. As stated earlier, such an approach is exactly equivalent to the unpaired bonding method provided that one maintains various restrictions of the present paper (e.g., common radial behavior for the  $\varphi$ 's and  $\chi$ 's appropriate to an antibonding-bonding pair on the one hand and to the unpaired bonding orbitals and antibonding holes on the other). In a less restricted treatment, the two approaches need not be equivalent but one is then involved with an unrestricted H-F theory and its associated difficulties.<sup>26</sup> Estimates of antibonding hole  $\gamma$  values involve *no* self-energy corrections [e.g., in Eqs. (44), (47), and (48)], and the results must equal (to second order) their unpaired bonding counterparts in order to maintain orthogonality requirements. Using Eq. (40) and the matrix elements and integrals of Tables III–VIII, we obtain values of  $\gamma$  equal to 0.014<sub>7</sub>, 0.048, and 0.024 for the  $e(s)$ ,  $e(\sigma)$ , and  $t^B$  orbitals, respectively. These are in remarkable agreement with the values listed in Table XI.

While we seem to have converged on “self-consistent” unpaired bonding values in Table XI, this by no means implies that they are in detailed agreement with what will be yielded by the more exact theory. On the other hand, they differ strikingly with those bonding-antibonding results obtained either by Sugano and Shulman or in Tables IX and X. This is due to the  $Ni^+ - Ni^{2+}$  Coulomb cancellation differences and will remain in the exact self-consistent field cluster theory.

In order to facilitate the discussion of 10  $Dq$  and transferred hyperfine effects, the  $\gamma$  values, appropriate to the unpaired bonding and antibonding models, have been extracted from Tables IX to XI and listed together in Table XII. The S&S III antibonding results are included for comparison, as are the  $\gamma^A$  values suggested by Table X, since these would be appropriate to 10  $Dq$  and the transferred hyperfine effects if we had adhered to the traditional (but incorrect) antibonding model. Different  $\gamma^A$  values are reported for 10  $Dq$  and for the transferred hyperfine effects as spin  $\downarrow$  parameters

are appropriate to the former and spin  $\uparrow$  to the latter in the antibonding model. Computed 10  $Dq$  or  $f_i$  values based on these  $\gamma^A$  will not be reported since this would be incorrect. We merely note that the use of these  $\gamma^A$ 's would predict even stronger covalent effects than those appearing in S&S III.

### A. Transferred Hyperfine Effects

Values of  $f_i$  were determined by using Eqs. (23) and (24) for the various sets of unpaired bonding  $\gamma_i$ 's reported (and defined) in Table XII. The separate spin  $\uparrow$  and spin  $\downarrow$  contributions to the  $f_i$  values are listed in Table XIII along with the experimental<sup>11</sup> values of  $f_i$ . The experimental  $f_s$  value includes the so-called 1s–2s cross-term correction.<sup>16,17</sup> Under the antibonding column, we list the S&S III predictions and give their pure overlap contribution separately from the covalent terms [cf. Eq. (20)].

The predicted  $f_s$  values are not in good agreement with experiment; the S&S III antibonding prediction is in somewhat better, but by no means good, agreement. What agreement there exists for the unpaired bonding results, arises largely from the spin  $\uparrow$  electron overlap term rather than from the spin  $\downarrow$  covalent terms.

The experimental  $f_\sigma$  value lies between the S&S III antibonding prediction and those of the present calculations. The theory is again seen to be in poor agreement with experiment. Quite aside from the fact that the S&S III predictions involve the inappropriate antibonding  $\gamma$ 's, we do not find them in marked numerical agreement with experiment. The present results consistently and appreciably underestimate both  $f_s$  and  $f_\sigma$ . We will see a similar, and perhaps related, low value for 10  $Dq$ . Let's consider that case now.

### B. Crystal Field Splitting Parameter

Our expression for 10  $Dq$  [Eq. (38)] was derived for the exact self-consistent Hamiltonian  $h$ , but, as discussed earlier, we shall use  $h_0$  matrix elements to estimate the diagonal, overlap, and covalent contributions. Before proceeding to this task, it is instructive to

TABLE XII. The  $\gamma$  values appropriate to the unpaired bonding and the antibonding models for 10  $Dq$  and the transferred hyperfine effects as obtained from Tables IX–XI. Included are the S&S III antibonding estimates.

	Unpaired bonding			Antibonding		
	A	B	C	D	E	
	Table IX	Table IX	Tables X, XI	S&S III	Table X	
	Eq. (40)	Eq. (39)				
For transferred hyperfine effects						
$\gamma_{s\downarrow}^B$	0.017 <sub>+</sub>	0.017 <sub>-</sub>	0.015	$\gamma_{s\uparrow}^A$	0.031	0.05–0.08
$\gamma_{\sigma\downarrow}^B$	0.066	0.065	0.047	$\gamma_{\sigma\uparrow}^A$	0.285	0.4–0.6
For 10 $Dq$						
$\gamma_{s\downarrow}^B$	0.017 <sub>+</sub>	0.017 <sub>-</sub>	0.015 <sub>4</sub>	$\gamma_{s\downarrow}^{BA}$	0.031	0.05–0.07
$\gamma_{\sigma\downarrow}^B$	0.066	0.065	0.047	$\gamma_{\sigma\downarrow}^{BA}$	0.285	0.2–0.5
$\gamma_{\pi\downarrow}^{BB}$	0.032 <sub>5</sub>	0.032 <sub>2</sub>	0.024	$\gamma_{\pi\downarrow}^A$	0.173	0.2–0.5

TABLE XIII. Comparison of unpaired bonding [cf. Eqs. (23) and (24)] and antibonding (S&S III) transferred hyperfine parameters,  $f_i$ , with experiment. The various calculations are defined as in Table XII.

$f_s$	Unpaired bonding			Antibonding S&S III
	A	B	C	
Spin $\uparrow$ overlap	=0.0021	0.0021	0.0021	Spin $\uparrow$ overlap =0.0022
Spin $\downarrow$ covalent	=0.0010	0.0010	0.0009	Spin $\downarrow$ covalent =0.0020
Total $f_s$	=0.0031	0.0031	0.0030	Total $f_s$ =0.0042
	Experiment=0.0054			
$f_\sigma$				
Spin $\uparrow$ overlap	=0.0037	0.0037	0.0037	Spin $\uparrow$ overlap =0.0041
Spin $\downarrow$ covalent	=0.0060	0.0059	0.0040	Spin $\downarrow$ covalent =0.0480
Total $f_\sigma$	=0.0097	0.0096	0.0081	Total $f_\sigma$ =0.0521
	Experiment=0.0378			

compare this estimate with the results appearing in S&S III. Such a comparison, however, cannot be done directly since their equation for 10  $Dq$  [S&S III, Eq. (2.11)] differs with Eq. (38). For example, they have an  $e_s$  overlap term,

$$-S_s \langle \varphi_e | h | \chi_s \rangle + S_s^2 \langle \varphi_e | h | \varphi_e \rangle \quad (54)$$

and a covalent contribution

$$-\gamma_s^{EA} \langle \varphi_e | h | \chi_s \rangle + S_s \gamma_s^{EA} \langle \varphi_e | h | \varphi_e \rangle. \quad (55)$$

Here, the second-order contributions appear in the "renormalization" term of their equation. Equations (54) and (55) obviously differ with lines 1 and 4 of Eq. (38) which are their counterparts here. Prior to comparing our results with S&S III, we must then ask whether the differing equations for 10  $Dq$  in any way affect our observations. With this in mind, we will first evaluate Eq. (38) with the antibonding  $\gamma$ 's and matrix elements of S&S III. [Equation (38) is readily converted for use in their antibonding model by replacing the values of  $\gamma$  and the matrix elements of the fifth line (for the  $t^{EB}$  electron) by the corresponding  $t^A$  values and similarly replacing the  $e_s^B$  and  $e_\sigma^B$  of the sixth and seventh lines by their counterparts  $e_s^{EA}$  and  $e_\sigma^{EA}$ , respectively.] The results of this calculation are given in Table XIV along with the values obtained by using Eq. (2.11) of S&S III, with and without second-order terms. Sugano and Shulman identified the linear terms, alone, as specific overlap or covalent contributions. With the inclusion of second-order terms, we see from Table XIV that the two equations yield the same *total* contribution from a particular electron but differ appreciably as to the relative roles of "covalent" and "overlap" effects. This implies that one equation or the other has incorrectly identified these contributions.

As already discussed, Eq. (38) was obtained from one-electron energy expressions [e.g., Eqs. (27), (28), and (30)] by the explicit evaluation of  $\langle \Psi | h | \Psi \rangle$ , a process which correctly yields the energy whether or not  $\Psi$  is an eigenfunction of  $h$ . The matrix elements of the resulting equations were then in no way manipulated. Equation (38) correctly yields a value of 10  $Dq$

in the limit of zero covalency by the simple expedient of setting the  $\gamma$  values equal to zero: the terms which remain are considered to be diagonal or overlap contributions; those which are introduced in the process of allowing nonzero  $\gamma$ 's are considered covalent effects. Thus, we conclude, Eq. (38) gives the proper breakdown of covalent and overlap effects.

Equation (2.11) of S&S III is based on one-electron energy expressions such as Eq. (29) which in turn was obtained from

$$\langle \varphi | h | \Psi \rangle / \langle \varphi | \Psi \rangle = \epsilon, \quad (56)$$

a relation which holds only if  $\Psi$  is an eigenfunction of the H-F equation [Eq. (6)], i.e., only for the *one* value of  $\gamma$  appropriate to that equation. One can alternatively obtain Eq. (29) by using Eq. (40) to remove a linear  $-(\gamma+S)\langle \varphi | h | \chi \rangle$  term from Eq. (27). However, in doing this, one assumes a specific relation between  $\gamma$ ,  $S$ ,  $\langle \varphi | h | \varphi \rangle$ ,  $\langle \varphi | h | \chi \rangle$ , and  $\langle \chi | h | \chi \rangle$ , namely, that  $\gamma$  be appropriate to the H-F solution. The resulting expression is simpler than Eq. (38), but it yields correct results only if the H-F  $\gamma$  value is inserted, and we can no longer correctly separate the covalent and overlap contributions by simple inspection, as we did for Eq. (38). From Table XIV we see that in S&S III the role of overlap effects was underestimated and that of covalency overestimated.

Computed unpaired bonding values for 10  $Dq$  are listed in Table XV: Cases A and B (described earlier) have been merged since they yield identical results; the S&S III antibonding values<sup>35</sup> of Table XIV have again been included for comparison. All of these results have been obtained by using Eq. (38) and all indicate

TABLE XIV. The overlap and covalent contributions to 10  $Dq$  obtained using Eq. (38) [modified as indicated in the text] and by using Eq. [S&S III, (2.11)] when evaluated with the matrix elements and  $\gamma^A$ 's of S&S III. All quantities are in  $\text{cm}^{-1}$ .

	Eq. (38)	S&S III Eq. (2.11)	
		Linear terms only	Linear plus second-order terms
<i>s</i> contributions			
overlap	2870	2070	2250
covalent	240	790	855
total	3110		3105
<i>p</i> $\sigma$ contributions			
overlap	4680	2400	2720
covalent	5035	6170	7000
total	9715		9720
<i>p</i> $\pi$ contributions			
overlap	-1535	-730	-905
covalent	-1440	-1680	-2075
total	-2975		-2980
Total overlap	6015	3740	4065
Total covalent	3835	5280	5780
Total	9850	9020	9845

<sup>35</sup> The total antibonding value for 10  $Dq$  differs by 70  $\text{cm}^{-1}$  with that appearing in S&S III. This occurs because we differ as to the matrix element appropriate to the second-order  $t_{2g}$  orbital contribution (see footnote 22).

TABLE XV. The diagonal (as estimated in S&S III), overlap and covalent contributions to  $10 Dq$  evaluated with Eq. (38) and the  $h_0$  Hamiltonian for the unpaired bonding  $\gamma$ 's of sets A-B and C, and for the antibonding  $\gamma$ 's of S&S III. All quantities are in  $\text{cm}^{-1}$ .

	Case A-B	Case C	S&S III
Diagonal	-3570	-3570	-3570
Overlap			
$e_{\sigma\downarrow}^{EA}$	3000	3000	2870
$e_{\sigma\downarrow}^{EA}$	4135	4135	4680
$t_{\downarrow}^A$	-1410	-1410	-1535
Total overlap	5725	5725	6015
Covalent			
Unpaired $e_{\sigma\downarrow}^B$	105	100	$e_{\sigma\downarrow}^{EA}$ 240
Unpaired $e_{\sigma\downarrow}^B$	725	665	$e_{\sigma\downarrow}^{EA}$ 5035
Unpaired $t_{\downarrow}^{EB}$	-170	-160	$t_{\downarrow}^A$ -1440
Total covalent	660	605	3835
$10 Dq =$	2815	2760	6280
Experimental $10 Dq = 7250$			

that overlap effects dominate. The covalent contributions play a small role in the present calculations and the resulting  $10 Dq$  values are observed to be substantially smaller than experiment.

Upon seeing such a disagreement with experiment, one might well inquire into the role played by uncertainties or errors in the  $\gamma$  values. From a given set of matrix elements (say, the unpaired bonding  $\langle |h_0| \rangle$ 's), an unpaired bonding  $\gamma$ , which is obtained variationally, gives the lowest one-electron (and in turn cluster) covalent crystal field energy obtainable for the orbital in question. Any deviation in the  $\gamma$  eigenvalues, for electrons appearing in the cluster ground state, will raise the ground-state energy, hence decreasing  $10 Dq$ . Any similar deviation for a  $\gamma^B$  will raise the excited state energy, thereby increasing  $10 Dq$ . If we utilize the unpaired bonding  $\langle |h_0| \rangle$  integrals, any variation in the  $\gamma_{\sigma}^B$  or  $\gamma_s^B$ , from the values of Table IX, will, therefore, decrease  $10 Dq$ , while a variation in  $\gamma_t^{EB}$  will increase it. Consider the effect of varying  $\gamma_{\sigma}^B$ , since it contributes the dominant covalent term in Table XV. If we assume Eq. (24) to be rigorously appropriate to the experimental  $f_{\sigma}$  value, we can obtain an experimental  $\gamma_{\sigma}^B$  which is four times the value appearing in Tables IX and XI. Inserting this into Eq. (38) yields a  $e_{\sigma}$  covalent term of  $\sim -1100 \text{ cm}^{-1}$  which, holding all other contributions constant, leads to a  $10 Dq$  of only  $\sim 1000 \text{ cm}^{-1}$ . Thus, a mismatch between a  $\gamma$  value and a set of matrix elements can severely affect a computed  $10 Dq$ . The behavior of these matrix elements determines the result; they could be of sufficient accuracy to yield qualitatively correct  $\gamma$  values while being quite unsatisfactory for an estimate of  $10 Dq$ .

As stated, Eq. (38) should be evaluated for the exact self-consistent Hamiltonian. In the absence of such computations, we can again gain some indication of the sensitivity of the results to matrix element behavior

by evaluating Eq. (38) for  $10 Dq$  with the bonding  $\langle \varphi | H | \chi \rangle^B$  matrix elements of Eq. (48). Replacing a  $\langle \varphi | h_0 | \chi \rangle^B$  integral by  $\langle \varphi | H | \chi \rangle^B$  affects both covalent and overlap contributions to  $10 Dq$ . The results of Table X indicate that  $\langle \varphi | H | \chi \rangle^B$  is smaller in magnitude than its partner  $\langle \varphi | h_0 | \chi \rangle^B$  for small covalent mixing (eventually reversing sign for greater covalency), and imply, in turn, a decrease in  $10 Dq$ . Using  $\langle \varphi | H | \chi \rangle^B$  values appropriate to the computed  $\gamma$ 's, decreases the covalent and overlap contributions by  $\sim 2000 \text{ cm}^{-1}$  and yields a  $10 Dq$  value  $\approx 800 \text{ cm}^{-1}$ , again increasing the numerical disagreement with experiment.

As was the case for the  $f_i$ 's, the present calculations yield a  $10 Dq$  which is appreciably less than experiment. These underestimates may be related; if so, more than a simple underestimate of  $\gamma$  values has occurred. We are involved with the more subtle, and more difficult, matter of matrix element behavior. Unfortunately, we have little evidence of whether a treatment involving the exact one-electron Hamiltonian, will or will not improve the numerical agreement with experiment. It is important to note that approximations were made<sup>10</sup> in estimating the  $V_L$  contributions to the  $\langle \varphi | h_0 | \chi \rangle$  and  $\langle \chi | h_0 | \chi \rangle$  matrix elements, but it is presently not obvious what repercussions, if any, these had on the results. This will be investigated in the future. Of greatest interest, of course, is the question of whether a treatment, such as the one outlined above, with the exact  $h$ , yields reasonable agreement with experiment. It need not.

## IX. OTHER PARAMETERS AFFECTED BY COVALENCY

Other parameters are affected by covalency, including the orbital reduction factors appropriate to the inter-electronic Slater  $F^k$  (or Racah  $B$  and  $C$ ) integrals of multiplet theory<sup>36</sup> and to  $g$  shifts and spin-orbit coupling,<sup>37</sup> and the determination of superexchange<sup>12</sup> interactions and neutron form factors.<sup>38</sup>

In the antibonding approach to the expectation value of a one-electron operator, Op, one compares  $\langle \Psi_i^A | \text{Op} | \Psi_j^A \rangle$  with the free ion  $\langle \varphi_i | \text{Op} | \varphi_j \rangle$  value. Quite often, a reduction factor defined by

$$k = \langle \Psi_i^A | \text{Op} | \Psi_j^A \rangle / \langle \varphi_i | \text{Op} | \varphi_j \rangle \quad (57)$$

is introduced to account for observed differences. Such a factor is, in principle, straightforward to obtain but is, in practice, almost never evaluated because of difficulties associated with the  $\langle \chi | \text{Op} | \varphi \rangle$  and  $\langle \chi | \text{Op} | \chi \rangle$  matrix elements. The one case where Eq. (57) has been evaluated occurs for Stevens' orbital reduction factor,  $k$ ,<sup>37,14</sup> appropriate to

$$\langle \Psi_i | l_m | \Psi_j \rangle = k_{i,j,m} \langle \varphi_{3di} | l_m | \varphi_{3dj} \rangle, \quad (58)$$

<sup>36</sup> See, e.g., J. C. Slater, *Quantum Theory of Atomic Structure* (McGraw-Hill Book Company, Inc., New York, 1960), Vol. I.

<sup>37</sup> K. W. H. Stevens, Proc. Roy. Soc. (London) **A219**, 542 (1953).

<sup>38</sup> J. Hubbard and W. Marshall (unpublished).

where  $l_m$  is some component of the orbital angular momentum  $\mathbf{l}$ . The  $\varphi\chi$  and  $\chi\chi$  contributions to  $k$  can be included and  $k$  tends to be less than one.

For other operators it is often assumed that the reduction effects are adequately predicted by the approximate relation

$$\langle \Psi_i^A | \text{Op} | \Psi_j^A \rangle = N_i N_j \langle \varphi_{3d_i} | \text{Op} | \varphi_{3d_j} \rangle, \quad (59)$$

where the  $N$ 's are the normalization constants of Eq. (2). The  $\langle \varphi | \text{Op} | \chi \rangle$  and  $\langle \chi | \text{Op} | \chi \rangle$  terms are neglected, because they are inconvenient to evaluate and are, hopefully, negligible. Detailed inspection of the Stevens' orbital reduction factor suggests that this approximation is inadequate. Nevertheless, necessity led Tinkham to rely on such a normalization estimate when discussing spin-orbit effects.<sup>14</sup> Sugano and Shulman also used this approach when dealing<sup>10</sup> with the experimentally observed<sup>11</sup> reduction of the Racah  $B$  and  $C$  integrals from their free ion values (here, the normalization enters in the fourth power because two-electron terms are involved).

In the (multielectron) unpaired bonding approach, the simple one-electron picture of the traditional model is lost. As discussed earlier, the overlap effects arise from the bonding-antibonding pairs and covalent contributions come from the unpaired bonding electrons. Now, if one ignores the  $[\varphi^*(\mathbf{r})\chi(\mathbf{r})]$  overlap density terms, overlap effects increase the charge and spin on the Ni<sup>2+</sup> ion. Covalent mixing also increases the charge but decreases the spin (i.e., increases minority spin). Our picture of reduction effects therefore depends on whether we are dealing with a charge or a spin-dependent effect.

The complications introduced by the multielectron considerations increase the size of the computations, but introduce no formal difficulties. When dealing with a diagonal one-electron operator matrix element one need only sum over paired bonding-antibonding, and unpaired bonding contributions. The neutron magnetic form factor is an interesting example of this case. For an off-diagonal matrix element [e.g., between the ground and excited states of Eq. (25)] we must remember that as one changes the occupation of antibonding orbitals, the bonding orbitals are also changed by the change in covalency [it was this which invalidated Eq. (26) as an expression for  $10 Dq$ ]. Such variations cause the orbitals of one state to lose their orthonormality with respect to orbitals of the other. These complications are easily managed computationally by using a formalism such as Löwdin's<sup>39</sup> for dealing with nonorthogonal functions or by evaluating the matrix element in terms of the antibonding holes ( $s$ ). The difficulties associated with  $\langle \varphi | \text{Op} | \chi \rangle$  and  $\langle \chi | \text{Op} | \chi \rangle$  matrix elements, mentioned above, also occur in the present approach. Detailed estimates of orbital reduction effects will not be at-

tempted in this paper. Let us briefly consider an example using the incorrect normalization correction to make an estimate of a reduction effect. In Sugano and Shulman's calculations, the competition between the overlap and the (dominant) antibonding covalent contributions, led to reductions in the Racah  $B$  and  $C$  integrals equal to those actually observed. If one were to consider such simple normalization corrections for the unpaired bonding results, one finds that the antibonding overlap terms lead to a 3 and 4% *enhancement* of the Racah  $B$  and  $C$  integrals and a negligible covalent contribution from the unpaired bonding electrons.

Similarly, the small magnitude of the unpaired bonding covalent mixing leads to poor agreement [using, say, Eq. (59)] with the various experimental " $k$ " values.

On several occasions in this section, we have cited difficulties associated with evaluating  $\langle \chi | \text{Op} | \varphi \rangle$  and  $\langle \chi | \text{Op} | \chi \rangle$  integrals. As this matter has implications for any more exact theory of crystal field effects, let us consider it briefly here. One is frequently interested in the highly singular  $r^{-3}$  operator appropriate to fine structure and hyperfine interactions. Matrix elements of this, and other, operators often nearly diverge because the LCAO wave functions were not required to have the proper singular behavior in the vicinity of each of the nuclei present (cf. the previous discussion of transferred hyperfine effects). Thus, even if the  $\langle \varphi | \text{Op} | \chi \rangle$  and  $\langle \chi | \text{Op} | \chi \rangle$  integrals are well behaved, their computed numerical values could be quite unrealistic. To our knowledge this matter has not been investigated and correcting for it promises to be a most interesting problem. Until this is done, one cannot claim complete quantitative understanding of the various orbital reduction effects.

## X. CONCLUDING DISCUSSION

A large number of observations, some major and some minor, have been made, concerning the application of the LCAO molecular orbital method to crystal field theory, in this paper. Perhaps the most important of these is the fact that it is the *unpaired bonding* electrons and not the antibonding electrons, which make covalent contributions to physical observables. The importance of this observation is largely due to the *intrinsic* (hence, quantitative) difference in the nature of the two types of covalent mixing (based on diagonalizing the one-electron Hamiltonian). In addition, we saw indications that a theory based on the incomplete Hamiltonian  $h_0$ , is internally inconsistent, hence inadequate. The results, obtained with  $h_0$ , were also seen to be in poor agreement with experiment, the covalent contributions being significant but by no means dominant. We are not optimistic that the same theory, evaluated with the exact H-F Hamiltonian, will recapture good agreement with all experimental parameters. (These observations are, of course, made for the molecular orbital theory. The alternative Heitler-London approach to the crystal field prob-

<sup>39</sup> P. O. Löwdin, Phys. Rev. **97**, 1474, 1490, 1509 (1955).

lem<sup>13</sup> is being studied by Rimmer and Hubbard.<sup>40</sup> The Heitler-London method introduces covalency through configuration mixing and thereby loses the simplicity of the single determinant description of the MO theory.)

The fact that the unpaired bonding orbitals make the only covalent contributions to an observable, is not surprising. It has been recognized for some time that, when dealing with Hartree-Fock single determinants, any mixing between a pair of *occupied* orbitals in no way affects the expectation value of an operator.<sup>36</sup> This immediately implies that the covalency of the simultaneously occupied orbitals of a bonding-antibonding pair, cannot in any way, affect the prediction of any observable, for the (NiF<sub>6</sub>) cluster states considered here.

Our understanding of orbital reduction effects and of the covalent "delocalization" of charge and spin differs in the two approaches. In particular, the covalency of a bonding-antibonding pair conserves charge on the metal ion while that of the unpaired bonding orbital involves a shift of charge from the ligands to the metal. Such differences in the *nature* of the two types of covalent mixing, have quantitative repercussions on the estimates of  $\gamma$  values (cf. Table XII). This is the most immediate quantitative reason for our preoccupation with unpaired bonding effects in this paper. As noted, the differences between computed paired and unpaired covalent mixing do not destroy the required spin symmetry of the cluster (i.e., it is an eigenfunction of  $S^2$ ). The unpaired bonding approach may be viewed as the proper application of *restricted* H-F theory to the current cluster model for KNiF<sub>3</sub>. Spin symmetry is maintained and what is more, if we apply the variation principle to the total energy of the cluster (with respect to the covalent mixing parameters), subject to the (RHF) requirement that the two types of covalent mixing be identical, one of necessity obtains the unpaired bonding (or antibonding hole) values. (The discussion for Cr<sup>3+</sup> has, of course, encompassed UHF theory and the breakdown of spin symmetry.)

We also noted that a theory based on the mixing of free ion metal  $\varphi$  and ligand  $\psi$  orbitals and based on the approximate Hamiltonian,  $h_0$ , appeared unsatisfactory (quite aside from the fact that quantitative agreement with experiment was not obtained) for we saw serious internal inconsistencies in the covalent mixing estimated for bonding-antibonding pairs. The effects did not seem so severe for unpaired bonding  $\gamma$  values, an observation which is probably misleading.

<sup>40</sup> D. Rimmer and J. Hubbard (unpublished), who use the configuration interaction method of Keffer *et al.* (Ref. 13).

Having failed to produce even fair agreement with experiment, the question arises whether the same theory, evaluated for the exact self-consistent Hamiltonian  $h$ , will or will not produce agreement with experiment. We do not expect the current (free ion  $\psi$  and  $\varphi$ ) cluster model to yield good agreement (say to 20%) for all the parameters considered in this paper. Should such a failure prove to be the case, there will again arise the old question of the variation of atomic orbital character away from the free ion behavior assumed in the present LCAO approach. Such a variation can take several forms: first, there is the matter of bulk expansion or contraction of the metal<sup>17,41</sup> ion (or ligands); secondly, there is the question of the extent to which  $3d\varphi_i$  and  $\varphi_3$  orbitals differ radially<sup>42</sup>; thirdly, there can be variation in orbital behavior from one multielectron state to the other; fourthly, one can allow different bonding and antibonding  $\psi$ 's to have different radial parts for their  $\varphi$  and  $\chi$  basis orbitals (involving us almost inevitably with a UHF theory); lastly, we have to consider the variation of orbitals centered on one nucleus when in the immediate vicinity of another, a matter important to orbital reduction and hyperfine effects. A bulk expansion of the metal  $\varphi$  orbitals may be expected with the covalent increase of charge occurring at the Ni site. This would improve numerical agreement with some experiments but it remains to be seen if this effect is fundamental to the current disagreement with experiment. Other questions which arise, include the role of correlation effects, one's ability to adequately define  $V_{\text{ext}}$  and the justification of the cluster model itself.

Finally, it is imperative that a proper crystal field cluster treatment, involving the exact Hamiltonian, be done. In this way, a number of the questions of the present paper would be resolved. We believe a calculation of this sort to currently be attainable with reasonable accuracy.

*Note added in proof.* In a recent publication, E. Šimánek and Z. Šroubek [Physica Status Solidi **4**, 251 (1964)] have considered unpaired bonding effects for the same system.

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<sup>41</sup> L. Orgel, J. Chem. Phys. **23**, 1824 (1955).

<sup>42</sup> Papers endeavoring to estimate this effect include R. E. Watson, Phys. Rev. **117**, 724 (1960); and R. E. Watson and A. J. Freeman, *ibid.* **120**, 1134 (1960). (There is an error associated with the cubic field term used in the first paper causing it to be approximately twice as strong as intended.)